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Waste Minimization Audit Report Case Studies of Minimization of Mercury-Bearing Wastes at a Mercury Cell Chloralkali Plant

Versar, Inc., Springfield, VA

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The report documents the results of waste minimization audits carried out, at two mercury cell chloralkali: plants in 1987. The audit addressed to waste streams, K-071-brine purification muds, and K-106- wastewater treatment sludges from Mercury cell processes in chlorine production. Several possible options are reviewed for each waste stream. Environmentally available treatment scheme identified re the most cost effective sollutions for both streams.

In addition to reporting in the results of the particular audit studies, the report also outlines the EPA recommended procedure for conducting waste minimization audits.

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WASTE MINIMIZATION AUDIT REPORT

Case Studies of Minimization of Mercury-Bearing Wastes at a Mercury Cell Chloralkali Plant

by:

Marvin Drabkin and Edwin Rissmann
Versar Inc.
Springfield, Virginia 22151

EPA Contract No. 68-01-7053
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Project Officer:

Mr. Harry Freeman
Hazardous Waste Environmental Research Laboratory
Cincinnati, Ohio 45268

HAZARDOUS WASTE ENGINEERING RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

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Foreword

The term, "waste minimization," is heard increasingly at meetings and conferences of individuals working in the field of hazardous waste management. Waste minimization is an umbrella term that includes the first four categories of the EPA's preferred hazardous waste management strategy which is shown below:

1. Waste Reduction: Reduce the amount of waste at the source, through changes in industrial processes.

2. Waste Separation and Concentration: Isolate wastes from mixtures in which they occur.

3. Waste Exchange: Transfer wastes through clearinghouses so that they can be recycled in industrial processes.

4. Energy/Material Recovery: Reuse and recycle wastes for the original or some other purpose, such as for materials recovery or energy production.

5. Incineration/Treatment: Destroy, detoxify, and neutralize wastes into less harmful substances.

6. Secure Land Disposal: Deposit wastes on land using volume reduction, encapsulation, leachate containment, monitoring, and controlled air and surface/subsurface water releases.

In general, the idea underlying the promotion of waste minimization is that it makes far more sense for a generator not to produce waste rather than develop extensive treatment schemes to ensure that the waste stream poses no threat to the quality of the environment.

In carrying out its program to encourage the adoption of waste minimization, the Hazardous Waste Engineering Research Laboratory has supported a program to carry out waste minimization audits in a wide variety of industrial settings. This report contains the results of waste minimization audits carried out at two mercury cell chlor-alkali plants. It will be useful to individuals interested in identifying opportunities for reducing those waste streams.

If further information is needed, please contact the Alternative Technologies Division of the Hazardous Waste Engineering Research Laboratory.

Thomas R. Hauser
Director
Hazardous Waste Engineering Research Laboratory

ABSTRACT

The USEPA is encouraging hazardous waste generators to develop programs to reduce the generation of hazardous waste. To foster such programs, the Agency's Office of Research and Development Hazardous Waste Environmental Research Laboratory (ORD/HWERL) is supporting the development and evaluation of a model hazardous waste minimization audit (WMA) procedure using the EPA hierarchy of waste minimization (WM) options, with source reduction being more desirable and recycle/reuse less desirable. Treatment options, although not considered WM, were evaluated if neither of the former alternatives was available. The procedure was tested initially in several facilities in 1986. WMAs were conducted at generators of a number of generic hazardous wastes, including corrosives, heavy metals, spent solvents, and cyanides.

In 1987, the HWERL WMA program has concentrated on ORD's top priority RCRA K and F waste list. Audits were conducted at generators of K071 and K106 wastes (mercury cell chloralkali plants), K048-K052 wastes (sludges and solids from petroleum refining), F002-F004 wastes (spent solvents), and F006 wastes (wastewater treatment sludges from electroplating operations). The present report covers WMAs carried out at two mercury cell chloralkali plants (designated as Plant No. 1 and Plant No. 2) seeking to develop WM options for K071 and K106 wastes.

The audit team was able to develop only one technically and economically viable source reduction option for K071 waste. Two treatment options (although not considered WM) appeared to be technically and economically viable for this waste, allowing it to be delisted by EPA and thus disposable in a local sanitary landfill. No viable source reduction or recycle/reuse options were available for K106 waste with one possible exception - a retorting process which appears capable of meeting delisting levels for mercury in the retorted K106 residue has been successfully tested by Plant No. 1.

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SECTION 1

INTRODUCTION

The national policy objectives established under the 1984 Hazardous and Solid Waste Amendments to the Resource Conservation and Recovery Act of 1976 include the goal of reducing or eliminating hazardous waste as expeditiously as possible. To promote waste minimization activities, the Hazardous Waste Engineering Research Laboratory (HWERL) of the U.S. Environmental Protection Agency (EPA), Office of Research and Development, has undertaken a project to develop and test a waste minimization audit (WMA) procedure. It is envisioned that such a procedure would be useful to generators of hazardous waste as they search for waste minimization alternatives.

A number of authors have recognized the potential value and desirability of conducting waste audits, although they have suggested differing approaches and scope limits for such audit activities (U.S. Congress 1986, USEPA 1986a, Fromm and Callahan 1986, Pojasek 1986, Kahane 1986, League of Women Voters, Mass. 1986). This HWERL project expands on a recently developed and tested audit procedure (EPA 1987, EPA 1987a, EPA 1987b) by conducting actual WMAs in cooperating industrial and government facilities. The present project includes audits at two industrial facilities, and is one of several current audit efforts being supported by HWERL.

Section 2 of this report presents the elements of an overall waste minimization program, of which the audit procedure is an important component. Section 3 describes the WMA procedure, its development, and its final recommended form. Section 4 presents the results of the WMAs performed at facilities that generate listed waste K071, and Section 5 contains the results of the WMAs performed at facilities that generate listed waste K106. Conclusions and recommendations resulting from these audits are presented in the respective sections.

SECTION 2

WASTE MINIMIZATION PROGRAM

Structured programs designed to improve the cost, energy efficiency, safety, and other environmental aspects of an industrial undertaking are not a new concept. During World War II, the General Electric Corporation developed standardized procurement procedures for reducing product cost without sacrificing functionality. Later, similar procedures were developed and applied to lower the costs of design and construction projects. This activity, known as value management, value engineering, or value analysis, is currently a well established government requirement. In fact, it was mandated by the U.S.EPA for all construction projects involving wastewater treatment plants. A subsequent study of 156 treatment plants showed that cost reduction programs saved $95 million, or a 12 to 1 return on investment (Zimmerman and Hart 1982).

Environmental compliance audits and reviews are also becoming more common and are acquiring the status of an industry norm. The primary objective of an environmental audit is to determine the status of a corporation's compliance with Federal, State, and local environmental laws and regulations (Truitt et al. 1983). Additionally, such audits often can provide information to aid risk assessment and corporate planning.

Energy conservation audits are performed to reduce energy consumption per unit production. It was estimated that energy audits helped save chemical process industries about $1 billion between 1974 and 1979 (Parkinson 1979). Other related structured programs include safety reviews, hazard analyses, or failure mode and effects analyses. Waste minimization programs can be considered to be in the same category as these programs.

The principal objective of a waste minimization (WM) program is to reduce the quantity and/or toxicity of waste effluents leaving the production process in a manner consistent with the goals of protecting human health and environment. Unlike environmental audit programs, a WM

program does not seek to determine or improve the regulatory compliance status of a facility. Rather, it is primarily oriented toward producing a set of effective measures to reduce waste generation.

Table 1 presents a breakdown of WM program elements. In the context of an overall WM program, the waste auditing process (composed of pre-audit, audit, and post-audit phases) follows the program initiation/planning phase. During this initiation/planning phase, the commitment of top management to reduce waste generation must first be established. This is often done with a formal directive signed by the chief executive officer of the firm or an administrator of a government organization. The organizational commitment to start a WM program is often associated with a goal setting process, e.g., duPont is currently implementing an annual 5 percent waste reduction goal.

A corporate WM program may be organized in a typical pyramid structure, with command and monitoring functions centered at the corporate level and implementation responsibility totally delegated to individual plants. A corporate-level independent expert task force may be formed to assist individual plants in setting up and executing their own WM programs.

At the plant level, the WM program may follow the scheme successfully used at Union Carbide for energy conservation efforts. At Union Carbide plants, a plant program coordinator is appointed and supported by a committee. The coordinator then selects and oversees individuals in each department who are responsible for devising and/or carrying out WM activities in their departments (Williams 1976).

This program planning phase should include the selection of audit teams to carry out the next program phase. The audit team leader should have a strong technical background, demonstrated problem solving ability, and, if possible, experience associated with the relevant process(es). In addition, the leader should possess strong management and communication skills. It would be preferable for the leader, or at least some members of the audit team, to have no previous association with the plant, so as to bring a fresh and unbiased perspective to the audit process. Such outsiders can be independent consultants or qualified personnel from other plants.

The audit team must have access to all required documentation and to a wide variety of plant personnel. During a recent internal workshop on waste minimization conducted by a major U.S. corporation, the participants (mostly environmental affairs managers at individual plants) were asked who should provide support to a waste audit team. The following responses were obtained:

Table 1. Waste Minimization Program Elements

Program phase	Job plan* phase	Elements
I. Initiation/ Planning		• Secure commitment/authority
		• Establish goals
		• Establish organization
II. Pre-Audit	Information	• Preparation for the audit
		• Pre-audit inspection
		• Waste stream selection
III. Audit	Creative	• Facility inspection
		• Generate comprehensive set of WM options
	Judgment	• Options evaluation
		• Selection of options for feasibility analysis
IV. Post-Audit	Development	• Technical and economic feasibility analysis
	Recommendation	• Report preparation
V. Implementation		• Selection of options for implementation
		• Design, procurement, construction
		• Startup
		• Performance monitoring

* Term adopted from value management program.

- Raw material suppliers;
- QA/QC department;
- Outside consultants;
- Customer representatives;
- Process engineer;
- Safety engineer;
- Materials engineer;
- Foreman;
- Plant manager; and
- Purchasing agent.

In short, the organization should be prepared to provide the audit team with access to a wide range of people both inside and outside the firm. The teams that carried out the audits described in this report were composed entirely of employees from outside consulting/engineering firms. Table 2 depicts the composition of the outside audit teams and the resident support groups.

The waste minimization auditing process (Table 1, phases II, III, and IV), which is described in detail in the next section, provides the key input to the implementation phase of the program, i.e., recommendations on which WM measures are to be implemented. Once a decision is made to proceed with the implementation of a specific WM measure, subsequent activities follow a well established, conventional pattern. Detailed design follows preliminary design; the procurement effort proceeds from inquiry and definitive bids to bid analysis and the expediting stages; and construction advances along the path determined by a detailed schedule and budget. The budget is controlled through estimates of cost performed at various project stages; accuracy increases as material and labor requirements become better defined. Startup follows mechanical completion. Finally, to ascertain the effectiveness of the changes made, ongoing performance monitoring is undertaken.

Table 2. Waste Audit Teams and Resident Support Groups for the Two Audits at Facilities Generating Listed Wastes K071 and K106

Plant No. 1 (Mercury Cell Chloralkali Plant)

1. Outside Audit Team

   Chemical engineer*, Ph.D., 37 yrs of experience

   Physical chemist, M.S., 20 yrs of experience

   Independent consultant**, Ph.D., Metallurgical Engineering, 40 yrs of experience in metallurgy, process, and environmental engineering

2. Resident Support Team

   Plant process engineer

   Plant environmental engineer

   Company main office staff environmental engineer

Plant No. 2 (Mercury Cell Chloralkali Plant)

1. Audit Team

   Chemical engineer*, Ph.D., 37 yrs of experience

   Physical chemist, M.S., 20 yrs of experience

2. Resident Support Team

   Plant environmental coordinator

   Plant process engineer

* Audit team leader.
** Technical support and review function only.

SECTION 3

WASTE AUDITING METHODOLOGY

As was shown in Table 1, waste minimization audits are a central feature of a WM program. The auditing process is subdivided into pre-audit, audit, and post-audit phases. The recommended sequence of steps shown in Table 1 (also shown in expanded form in Table 4), is based on modifications of the originally proposed sequence, which is presented in Table 3. Modifications were made to reflect the experience and insights gained as a result of actual audit work. The following sections detail each of the eight sequential steps of the recommended waste minimization audit (WMA) procedure shown in Table 4.

PREPARATION FOR THE AUDIT

The objective of this activity is to gain background information about the facility to be audited. Preparation should include examination of literature references related to the activities performed at the facility, such as EPA background documents on the industries involved, plant permit applications, and other relevant documents pertaining to waste discharge at the industrial facilities of interest. Proper preparation should result in a well-defined needs list, inspection agenda, or a checklist detailing what is to be accomplished, what questions or issues need to be resolved, and what information should be gathered.

For the host facilities audited in this report, the needs list (Table 5) was provided to the resident support team in advance of the site visit. This was very important in ensuring the success (and efficiency) of the site visit, since it provided time for the facility personnel to assemble the materials required by the audit team prior to its visit. A more generalized list of documents and information sources is given in Table 6.

In the audits of the three facilities reported herein, the availability of the required process documentation was excellent. This documentation proved to be invaluable in enabling the audit team to establish a set of waste minimization options.

Table 3. Initially Proposed Waste Minimization Audit Procedure

Job plan element	Step
Information phase	1. Preparation for inspection
	2. Facility inspection
	3. Process and waste stream description
Creative phase	4. Generation of WM options
Judgment phase	5. Preliminary evaluation and ranking of options
	6. Presentation, discussion, and joint review of options with plant personnel
	7. Selection of options for feasibility analysis
Development phase	8. Technical and economic feasibility analysis
Recommendation phase	9. Final report preparation

Table 4. Recommended Waste Minimization Audit Procedure

Program phase	Activities	Product
Pre-Audit	1. Preparation for the audit	• needs list/ inspection agenda
	2. Pre-audit meeting and inspection	• notes
	3. Waste stream selection	• process description
		• waste descripton with rationale for selection
Audit	4. Audit inspection	• notes
	5. Generation of a comprehensive set of WM options	• list of proposed options with written rationale
	6. Options evaluation and selection for feasibility analysis	• list of selected options
		• options ratings by audit team and by plant personnel
		• options interim report
Post-Audit	7. Technical and economic feasibility analysis	study or budget grade estimates of capital and operating costs; profitability analysis
	8. Final report preparation	final report with recommendations

Table 5. Waste Minimization Audits - Information Needs List for Listed Wastes K071 and K106 at Plants No. 1 and 2

1. Process Flow Diagrams (PFDs) with Heat and Material Balances (HMBs).
2. Piping and Instrumentation Diagrams (P&IDs).
3. Plot plan or general arrangement of equipment.
4. Process description (process flows, liquid and solid wastes characterizations).
5. Equipment layouts (plan and elevation views).
6. Quantities and costs of chemicals.
7. Dimensions and operating gallonage of all pertinent process vessels and tankage.
8. Quantities and costs of disposal for all wastes (liquid and solid).
9. Process equipment materials of construction.
10. History of previous waste management projects and any related documentation.

Table 6. Waste Minimization Audits Generalized List of Information Sources

- Design process flow diagrams (PFD) with heat and material balances (HMB) for process and pollution control systems
- Equipment list
- Piping and instrument diagrams (P&ID)
- Materials application diagrams (MAD)
- Plot and elevation plans
- General arrangement drawings
- Piping layout drawings
- Operation manuals, process descriptions
- Permits and/or permit applications
- Emission inventories
- Hazardous waste manifests
- Annual (or biennial) reports
- Waste assays
- Operator data logs, batch sheets
- Materials purchase orders
- Environmental audit/review reports
- Production schedules
- Organization chart

Experience with other sites indicates that the availability and quality of information varies significantly, however. It is important to allow for this contingency and to have a fall-back position. For example, if a piping and instrument diagram (P&ID) is not available, it may be possible to obtain a piping layout plan instead. Similarly, if the information cannot be obtained from the facility, that does not mean that it is unavailable elsewhere. Much information is obtainable from outside vendors, e.g., the costs of bath make-up chemicals or the physical design of the process equipment. If information is truly needed, it can be obtained with proper initiative and ingenuity, although such action may affect project costs and schedules. In light of this possibility, it is important to seek only that information which is necessary to understand the process, to allow for delineation of waste sources and current waste management techniques, and to characterize waste generation quantitatively. Requesting unnecessary information burdens both the provider and user (auditor) and slows down the work.

HOST SITE PRE-AUDIT SITE VISIT

The purpose of this meeting is to become familiar with plant operations and plant personnel. Initial contacts with plant personnel should include solicitation of their views on the focus and function of the audit. This will help to identify waste streams of concern to the facility. The information needs defined in the previous step should be discussed here and hopefully met. A guided tour of the facility should be taken.

At this initial visit, the groundwork for a successful working relationship with facility personnel must be laid. It should be stressed that a cooperative attitude and active involvement by host facility personnel are essential to the success of the audit process. The initial point of contact at the facility (Plant Manager, Environmental Coordinator, etc.) must be enlisted as a "Product Champion" for the program before the audit commences. He/she must be encouraged to relay the message of cooperation and involvement to others at the facility.

WASTE STREAM SELECTION

Suitable waste streams should be selected either following the initial conference with plant personnel or after the first plant inspection. Selection should be based on discussions with plant personnel and on the independent assessment of the project team. The criteria used to select a waste stream must include at a minimum:

- Composition;
- Quantity;

- Degree of hazard (toxicity, flammability, corrosivity, and reactivity);
- Method and cost of disposal;
- Potential for minimization and recycle; and
- Compliance status.

For the two case studies cited in this report, stream selection was not a problem. Focusing the audits on two particular wastes (listed wastes K071 and K106) simplified the selection. Both mercury cell chloralkali facilities generate only these two hazardous wastes in any appreciable quantity.

With the selection of the waste streams, the pre-audit stage of the procedure is completed. At this point, it is recommended that a written description be prepared of the facility, process, or operation and of the waste streams. The description should encompass:

- Facility location and size;
- Description of operations or processes of concern, including diagrams necessary to detail the pertinent aspects of waste generation; and
- Waste stream(s) description centering on sources and current methods of management; this information should be supplemented with summaries of generation rates, compositions, disposal costs, and raw material costs, and the rationale for waste selection should be provided.

Descriptions of facility, process, and waste stream(s) for the facilities involved with audits on listed wastes K071 and K106 are given in Sections 4 and 5. Such descriptions summarize all the pertinent information acquired.

HOST SITE WASTE MINIMIZATION AUDIT VISIT

In the course of the pre-audit activities, a general understanding of the process facility operations and, more important, of waste sources was established. Also, waste stream selection had been finalized (in most cases) and the information summarized in a written description of the facility, process, and waste stream(s).

With the needed comprehension of the process and focus in place, the audit inspection can now be conducted. Typically, the inspection would focus on selected aspects of the operation identified through the pre-audit activities. The governing objective is to obtain a greater awareness of the principal and secondary causes of waste generation and to examine the items overlooked in the pre-audit stage.

The audit inspection is the ultimate step in the information gathering process. The following guidelines have been formulated as a result of the work performed on this project:

1. Have an agenda ready. This should cover all points that still require clarification following the pre-audit phase.

2. Plan on inspection of the various process operations of interest at different times during the production shift for continuous processes, in order to observe possible fluctuations in normally steady state operations. Expect to monitor operations over a period of one to two days.

3. Obtain permission to interview the operators, eight-hour shift supervisors, and foremen directly. Listen attentively and do not hesitate to question more than one person if the answer is not forthcoming. Try to assess the operators' and their supervisors' awareness of waste generation aspects of the operation. Note their familiarity (or the lack thereof) with the impacts their operation may have on other operations, e.g., the effect of dumping spills of mercury-bearing brine into the existing wastewater treatment plant at the chloralkali facility, rather than metering these solutions at a controlled rate.

4. Obtain permission to photograph the facility. Photographs are especially valuable in the absence of plan layout drawings. Many details can be captured in photographs that otherwise could well be forgotten or inaccurately recalled at a later date.

5. Observe the "housekeeping" aspect of the operation. Check for signs of spills or leaks. Ask to visit the maintenance shop and inquire about their problems in maintaining the equipment leak-free. Assess the overall cleanliness and order of the site.

6. Assess the level of coordination of environmental activities among various departments.

During the planning stage and the actual audit inspection itself, it is beneficial to mentally "walk the line" from the suspected source of waste generation to the point of exit, be it a treatment unit, storage facility, or haulage to offsite RCRA treatment, storage, and disposal (TSD) facilities. The audit inspection must result in a clear understanding of the causes of waste generation.

GENERATION OF WM OPTIONS

Thus far, the audit process has been mainly oriented toward information gathering and organization. These activities should have yielded a thorough understanding of the origins of waste generation and of the process or facility operations in general. The audit activity has now reached the creative phase.

The objective of this step is to generate a comprehensive set of WM options. Such activity may take the form of a "brainstorming" session involving audit team members or may involve separate efforts by individual members. A combination of these approaches was found to be of value during the audits conducted for this study. In this stage of the audit process, it is important to generate as many options as possible. Current WM measures in the audited facility should also be listed. This knowledge often leads to the formulation of additional options and provides valuable insights for the option evaluation step to follow.

In generating options, most of the effort should first focus on source reduction, followed by recycling and then treatment (if there are no options available in either of the preferred areas). Such a hierarchy of effort stems from the fact that environmental desirability favors source reduction over recycling and recycling over treatment.

Current EPA-proposed definitions of waste minimization and key waste minimization terms are given in Figure 1. A generalized guide map to various source reduction elements is shown in Figure 2. For a discussion of the terms and examples illustrating each element, the reader is referred to the EPA support document for the 1986 Report to Congress on Waste Minimization (USEPA 1986b).

To develop options, it is often necessary to examine the technical literature. The reference section of this report lists the sources consulted for technical material relevant to reduction or elimination of mercury cell chloralkali mercury-bearing wastes. Options can also be formulated through discussion with manufacturers of equipment or suppliers of process input materials.

The result of the WM options generation step should be a list identifying each option, together with a brief description of the rationale for its listing. For the K071 waste studied in this report, a total of nine relevant options could be determined at both the facilities audited, while for the K106 waste, a total of five relevant options were developed at both facilities.

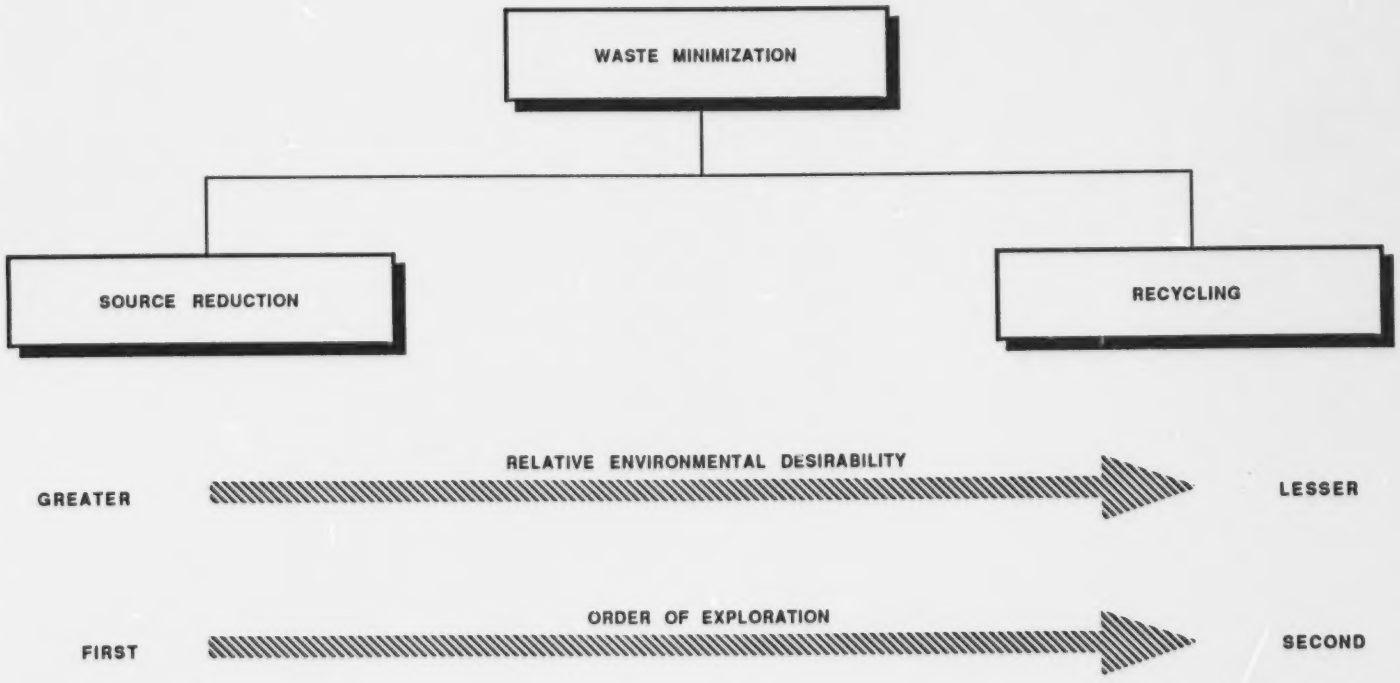

FIGURE 1. COMPONENTS OF WASTE MINIMIZATION, THEIR HIERARCHY AND DEFINITIONS

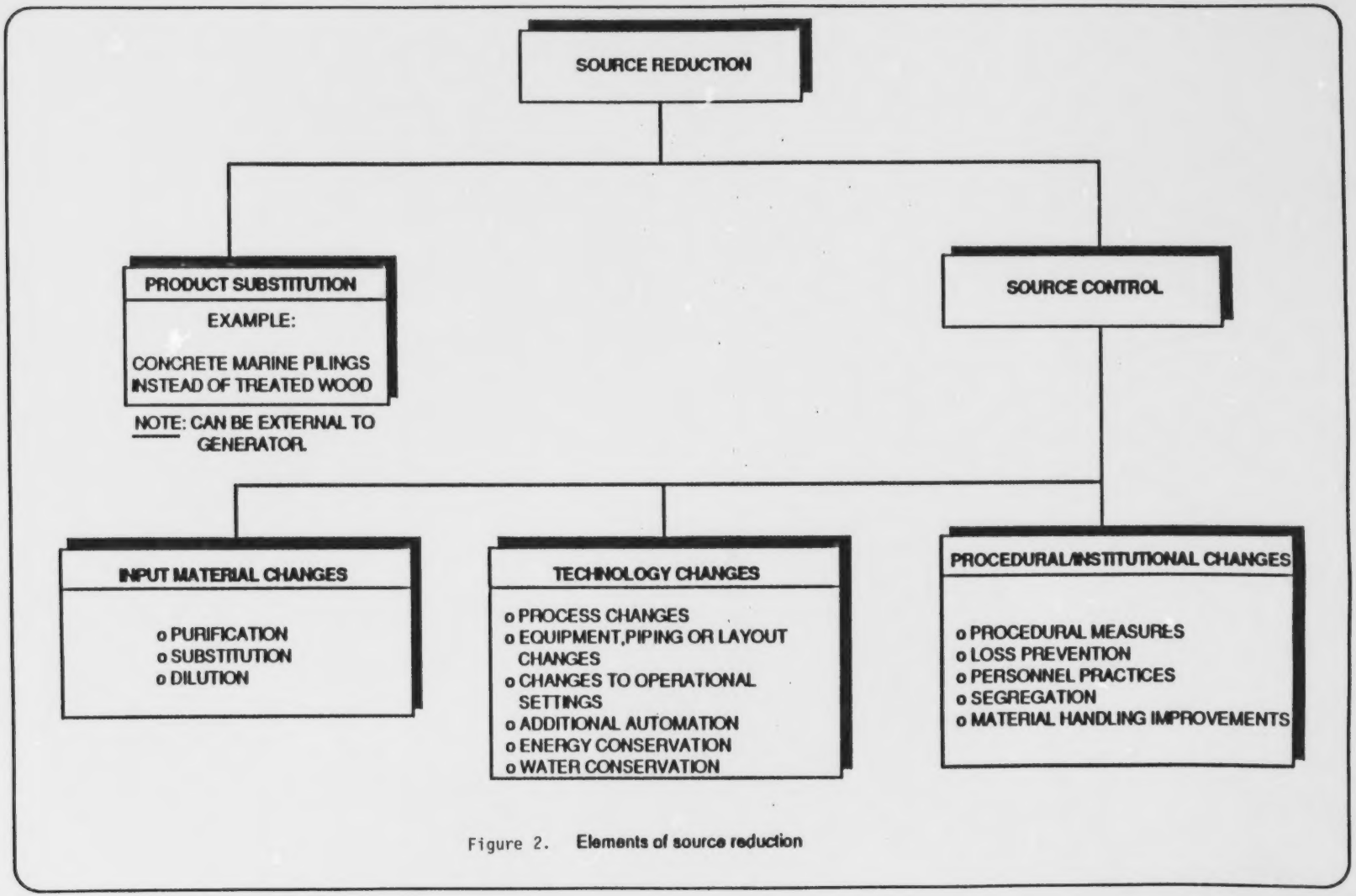

Figure 2. Elements of source reduction

PRELIMINARY EVALUATION AND RATING OF OPTIONS

Each of the options postulated in the preceding step must undergo a preliminary engineering evaluation and rating. The objective of this evaluation is to eliminate the measures that do not merit additional consideration and to rank the remaining measures in order relative to their overall desirability.

The evaluation should include, at a minimum, consideration of the following aspects:

- Waste reduction effectiveness (i.e., reduction of waste quantity and/or toxicity);
- Extent of current use in the facility;
- Industrial precedent;
- Technical soundness;
- Cost (preliminary capital and operating cost evaluation). An important economic yardstick for option evaluation is the determination of a "payback period," which is defined here as the incremental investment divided by the net savings in direct operating costs due to implementation of the proposed option.
- Effect on product quality;
- Effect on plant operations;
- Implementation period; and
- Resources availability and requirement.

The preliminary evaluation and valuing process would consist of the following steps carried out by the audit team:

(a) Developing a written rationale for each proposed option including a clear description of the operating principle, estimates of waste minimization measured in pounds of waste and in pounds of waste per unit production, estimates of potential resource recovery measured in pounds of waste component recyclable to the process or salable as a recovered material, perceived advantages and disadvantages, simplified schematics of the proposed material flow, material balance calculations, "order of magnitude" cost estimates, references relating to prior applications, and other relevant documentation pertaining to the idea. These steps were carried out as appropriate for each option developed for minimization of listed wastes K071 and K106.

(b) Qualitative rating of each option in three categories: waste reduction effectiveness, extent of current use, and future application potential. The ratings are to be done on scale of 0 to 10 by a proponent, then reviewed by the audit team leader.

It is expected that some options may receive ratings low enough to warrant their withdrawal. The team leader may call a review meeting to submit the ratings to a collective discussion or vote. In the case of the audits discussed in this report, a number of such options were withdrawn, as is discussed in Sections 4 and 5.

The product of this effort should be a table summarizing the preliminary ratings for each option that addresses a particular waste stream or source, along with the written documentation developed in this phase of the audit. Table 7 is a sample table illustrating the approach used to develop such a summary table.

PRESENTATION AND JOINT REVIEW OF OPTIONS WITH PLANT PERSONNEL

Following the technical and economic evaluations of the selected options by the audit team, these options are prepared in the form of a Preliminary Audit Report to be submitted to appropriate plant personnel. Each option in the Preliminary Audit Report should be well described in terms of the technical rationale and projected "order of magnitude" cost estimates. Cost estimates are of particular importance to plant personnel who have to deal with tight operating budgets and must have some idea of the cost of implementing an attractive-appearing option. In this regard, calculation of "the payback period" will provide a quick indication of the economic viability of the proposed option. Cost estimates are also of importance to the options belonging to the category of good operating practices. Availability of preliminary cost data along with the presentation of this category of option circumvents quick dismissal of these options as "trivial" by a technology-oriented plant engineer.

The plant personnel should then be asked to review the Preliminary Audit Report and independently rate each proposed option, revise them based on their assessment, and incorporate any additional options they consider applicable.

The review process would culminate in a joint meeting in which the audit team would present the proposed options one by one. The presentation ideally should include a detailed discussion of the rationale and reasons for selected ratings. The plant engineers would then present their critique or comments. The discussion should conclude with a revised rating acceptable to both sides. If such a conclusion cannot be reached, a further course of action must be well outlined.

Table 7. Summary of Source Control Methodology for the A/B Powder Formulation Process: Illustration of Development of Options Ranking

Waste source	Control methodology	Waste reduction effectiveness	Extent of current use	Future application potential	Fraction of total waste	Current reduction index	Future reduction index
Weighing operation	1. Return empty containers	2	0	2		0.00	0.25
	2. Use preweighed containers	2	0	4		0.00	0.50
	3. Use drum covers	2	2	1		0.25	0.06
	Overall	2.00	0.67	2.33	0.10	0.25	0.50
Wet grind loading and unloading	1. Use plastic funnel/collar on unit	2	0	4		0.00	0.50
	2. Use smaller trays, manual operation	2	0	2		0.00	0.25
	3. Place trays on rack, walk-in oven	2	0	2		0.00	0.25
	4. Use elevator table on rack, walk-in oven	1	0	1		0.00	0.06
	5. Install roller conveyer under valve	1	0	1		0.00	0.06
	6. Install fail-close valve on discharge	2	0	3		0.00	0.38
	7. Pump slurry into trays over at oven	2	0	1		0.00	0.13
	8. Reduce cleaning frequency	3	0	3		0.00	0.56
	9. Bypass dry grinding unit	2	0	4		0.00	0.50
	Overall	1.89	0.00	2.33	0.45	0.00	0.56
Dry grind loading and unloading	1. Use plastic funnel/collar on unit	2	0	4		0.00	0.50
	2. Do not load while unit is operating	3	4	0		0.75	0.00
	3. Inspect all seals regularly	2	3	2		0.38	0.06
	4. Use drum covers	2	2	3		0.25	0.19
	5. Bypass dry grinding unit	4	0	4		0.00	0.90
	Overall	2.60	1.80	2.60	0.45	0.75	0.90
All sources	All methods				1.00	0.58	0.71

The objective of the meeting is to obtain an agreement on the ratings of various proposed options; these ratings would then be analyzed and used to rank all the options, with the aim of selecting those that warrant further evaluation by the plant. It also may happen that the plant personnel may suggest new options or that such options may result from the joint discussion.

Following the meeting, all appropriate revisions of the options presented in the Preliminary Audit Report would be made in preparation for the issuance of a Final Audit Report.

In the present audit effort, both the audit team and the plant personnel were in agreement on the evaluation of each of the options presented.

FINAL AUDIT REPORT

In accordance with the workplan, the Final Audit Report will contain, at a minimum, the following sections:

1. Facility and process description;

2. Description of waste stream(s) origin, composition, and quantities;

3. Detailed description of all work minimization options considered, including simplified schematics of revised process flows (if appropriate) and lists of any new process equipment required;

4. Detailed evaluation of technical feasibility and potential benefits of all waste minimization options considered, together with their preliminary economics (capital and operating costs, estimated payback period) and final rankings (based on audit team findings and host plant engineers evaluations); and

5. Recommendations including any research and development efforts needed to further evaluate the recommended options.

WASTE AUDITING - SOME DO'S AND DON'TS

Some of the most important lessons learned in the pilot audits relate to the human element of the audit process, i.e., to the interaction between the audit team and the host facility personnel.

Obviously it is vital that host facility personnel become and remain active participants throughout the audit process. Some non-technical skills of the audit team personnel, and particularly of the audit team leader, were found to be extremely valuable here.

The audit team leader must be an effective and aggressive communicator as well as a technical expert, because this individual must serve as a facilitator for the audit team and host facility personnel alike. A reserved and low key attitude and behavioral style by the audit team could lead to a passive or disinterested stance by the host facility personnel.

The experience gained in these audits also led to a modification of the audit method. The modified approach requires host facility personnel to independently develop ratings for each of the waste reduction options under consideration. The audit team's ratings for the options and the host facility's independent ratings can then be reviewed and reconciled in a group session. The initial approach of having the host facility personnel merely review and discuss the audit team's ratings following the presentation of the option ratings resulted in relatively casual, uninvolved behavior by the host facility staff.

The pre-audit activities, particularly the pre-audit site visits, were found to be extremely important in facilitating the audit process. When the audit team spent a little more time getting to know the host facility staff and the functioning of the organization, the audit process moved more smoothly. The audit team found it easier and faster to acquire needed data, because the members knew the operation and the people a little better, and the level of cooperation by plant staff was improved.

In summary, a WMA (and a WM program as a whole) requires that audit team members exhibit effective communications and human interaction skills, as well as technical insight and engineering ability. A successful WM audit program thus requires success in both technical and human relations areas.

SECTION 4

LISTED WASTE K071 - WMA CASE STUDIES

The focus of this set of case studies is to propose ways to reduce or eliminate the generation of listed waste K071. This waste is defined in 40 CFR 261.32 as follows:

- K071: Brine purification muds from the mercury cell process in chlorine production, where separately prepurified brine is not used.

Two facilities were selected as host sites for WMAs at generators of listed waste K071. The two plants involved are mercury cell chloralkali facilities located in the Southeast. Background information on the generation of listed waste K071 at mercury cell chloralkali plants can be found in two Environmental Protection Agency (EPA) documents on this waste (EPA 1980, EPA 1980a). In this report, the two plants studied are designated as Plant No. 1 and Plant No. 2.

WMA AT PLANT NO. 1

Facility Description

Plant No. 1 is a mercury cell chloralkali facility located in the Southeast and has a name plate capacity of 138,000 metric tons of chlorine per year. The facility operates two parallel mercury cell electrolytic process production lines - one manufacturing sodium hydroxide (NaOH) as a co-product and the other producing a potassium hydroxide (KOH) co-product. The capacities of the two parallel production lines are 310 metric tons of NaOH per day and 246 metric tons of KOH per day.[1]

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[1] In subsequent sections of this report, reference is made to the sodium and potassium hydroxide production facilities, with chlorine being understood as the co-product in both cases.

The facility uses DeNora type mercury electrolytic cells, some of which are used for NaOH manufacture and the balance for KOH production.[1] All cells have been equipped with metal anodes since the late 1960s.[2]

The facility is located near a major river and receives its raw materials by barge and railcar. Rock salt from Louisiana is received by barge and stored in outdoor piles prior to use. Potassium chloride from Canadian sources arrives by rail and is stored in railcars prior to use.

The facility production is almost entirely merchant (i.e., all of the products produced are sold to other facilities except for a portion of the produced K071, which is used internally to produce anhydrous potassium carbonate (K_2CO_3)). Chlorine (Cl_2), caustic soda (NaOH), KOH, and hydrogen are the only products of the electrolytic process. Most customer facilities for the Cl_2, NaOH, and KOH are located in the Southeast. During the winter months, by-product hydrogen is combusted in the plant boilers generating a portion of the facility's steam requirements. At other times of the year, part of the hydrogen is sold over the fence.

Plant No. 1 presently generates a total of about 2,500 tons per year of listed waste K071 (mercury-bearing brine purification wastes) from both the sodium and potassium hydroxide production lines, as well as approximately 2,500 tons per year of listed waste K071 (mercury-bearing saturator insolubles) from the NaOH production line. All of these wastes are currently sent offsite to a hazardous waste landfill.

Process Description

Plant No. 1 produces both sodium and potassium hydroxides, along with a chlorine co-product in parallel electrolytic mercury cell production lines. During electrolysis of sodium chloride brine in the mercury cells, chlorine gas is formed at the anodes and is collected, cooled, and dried by passing through sulfuric acid and then compressed, liquified,

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1 The present DeNora electrolytic mercury cell design was developed by Dr. Annunzio DeNora, an Italian technologist, in 1968, and has become the industry standard for the manufacture of chlorine by electrolysis of brine using mercury cells. In this cell, a stream of flowing mercury is used as the cathode, and specialty-designed metal plates are used as anodes.

and stored for shipment. Simultaneously, in the cells, a sodium-mercury amalgam is formed at the flowing mercury cathodes. Mercury leaving the cells, which contains the amalgam, is subsequently reacted with water in units called denuders. The reaction converts the amalgam to mercury metal, a 50 percent NaOH solution, and hydrogen gas. The hydrogen gas is collected and partially sold and partially burned for fuel; the NaOH solution is further processed before being shipped to customers, and the mercury is returned to the cells. Figure 3 is a simplified schematic of the NaOH/chlorine production process.

The spent brine leaving the mercury cells (at about pH 5) contains about 22 percent sodium chloride, versus 25 percent in the incoming brine. This depleted brine typically containing 6 ppm dissolved mercury[1] is further acidified with hydrochloric acid (to pH 2.5) and is then dechlorinated using vacuum flash tanks. The chlorine released is collected and combined with that generated in the mercury cells for further processing. The dechlorinated brine is then pumped to the initial portion of the process, where rock salt is added to form a resaturated brine. Table 8 presents a typical rock salt analysis at Plant No. 1. The brine has NaOH solution blended with it prior to entering the dissolver. The NaOH addition adjusts pH from ~2.5 to 10.5 to 11 in order to avoid dissolution of silica (as silicates) in the brine. Rock salt (NaCl) dissolution occurs in a saturator (or dissolver) tank, where the flow of salt is countercurrent to the brine flow. No agitation is used in the dissolver tank. In this operation, the sodium chloride dissolves in the brine and the insolubles present in the rock salt fall to the bottom of the saturator vessel, from where they are periodically removed by mechanical means and discharged to the brine recovery pads (concrete-lined sludge pads for collecting K071 waste sludges and decanting and recycling excess brine from these wastes). These insolubles constitute the largest portion of K071 waste and include insoluble clay and mineral components of the salt feed, together with precipitated materials formed in the dissolution step and small amounts of entrained mercury. The dissolution of the salt occurs in brine at a temperature of about 70°C.

Plant No. 1 has five dissolver tanks in parallel, two of which are in use at any given time, one of which is on standby, and a fourth, which is undergoing cleaning to remove collected insolubles (which form a rock-like mass on the sides and the bottom of the tanks as they accumulate). Operation of the fifth dissolver is described below. The dissolver tanks are 35 feet in height and 30 feet in diameter, and are cone-shaped at the base.

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1 The mercury can be in as many as three ionic forms: Hg^{+}, Hg^{++}, and $(HgCl_4)^{=}$.

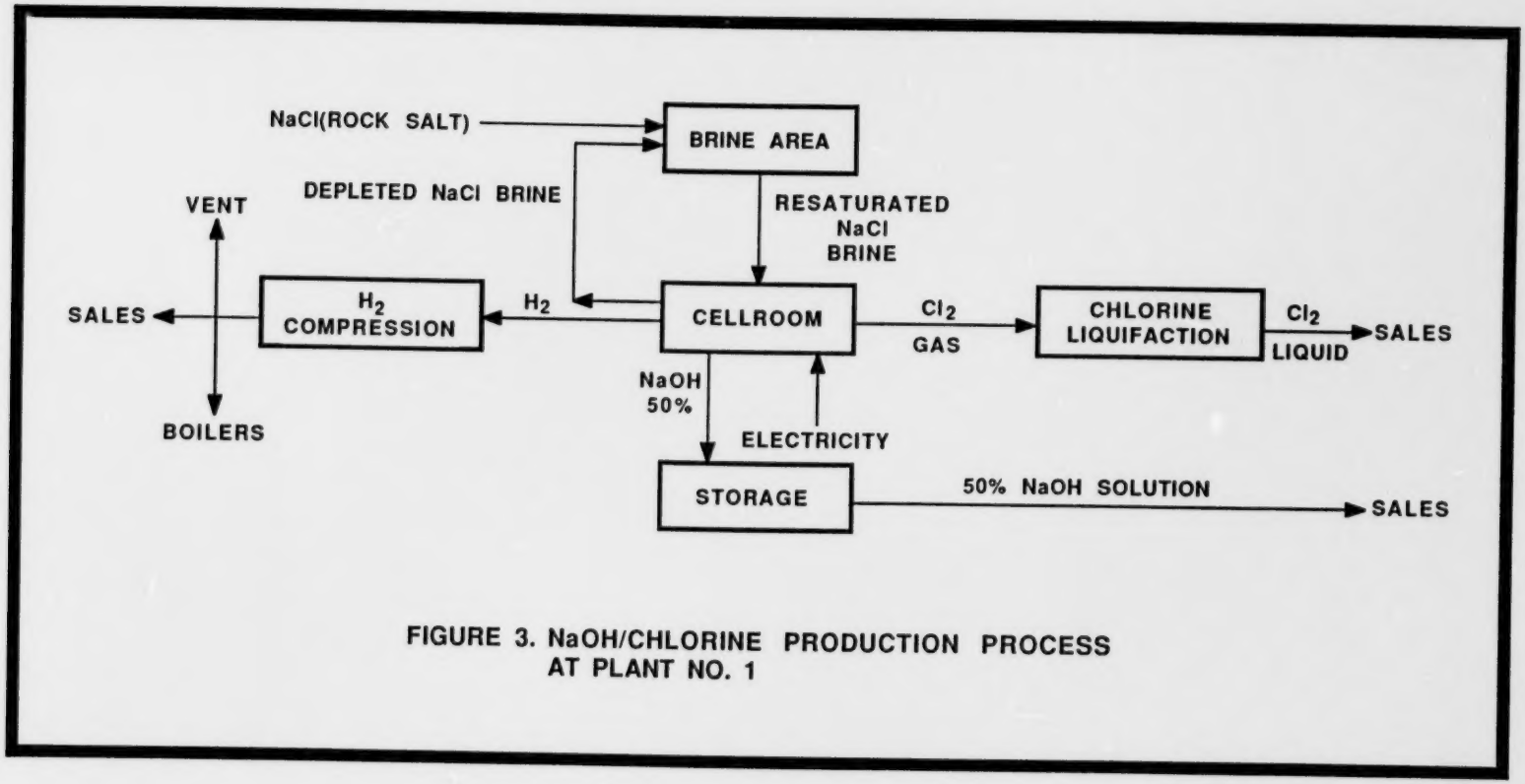

FIGURE 3. NaOH/CHLORINE PRODUCTION PROCESS AT PLANT NO. 1

Table 8. Typical Rock Salt Composition at Plant No. 1

Compound	Weight percent
Water Solubles	
NaCl	98.5
$CaSO_4$	1.3
Insolubles	0.2
Acid Solubles	
NaCl	98.5
$CaCO_3$	0.01
$CaSO_4$	1.5
Insolubles	0.00
Mg	38 ppm
Fe	<10 ppm
Si	<10 ppm

Source: Plant No. 1 in-house data.

The resaturated brine is next pumped to a treatment tank where sodium carbonate is added. Calcium, magnesium, and iron ions present in the brine precipitate as calcium carbonate and magnesium and iron hydroxides, respectively. These precipitates are removed in the treated brine clarifier. The clarifier overflow is then passed through sand filters to remove residual solids. The underflow, containing the precipitated solids and small amounts of entrained mercury (a second form of K071 waste), is fed to concrete-lined sludge pads, where the solids settle.

The clarification and filtration operations are carried out at 60 to 70°C. The clarifier used is 90 feet in diameter and 15 feet in height. The sand filters operate in the downflow mode, and are periodically backwashed with brine to flush out accumulated impurities. The backwash stream is sent to the K071 waste sludge pads, where the solids settle and the clean brine is returned to the clarifier.

The fifth dissolver tank operates in the "hot-process" mode; i.e., when the brine flow rate through the system clarifier reaches its capacity, this dissolver is put into operation as both a brine preparation and an impurities precipitation tank. Sodium carbonate is added to resaturated brine in this dissolver, causing precipitation of impurities in the added salt as insoluble carbonates, e.g., calcium carbonate. The treated brine from this tank is pumped to the sand filters and the settled solids are discharged to the K071 sludge pads.

The purified brine after filtration is acidified with hydrochloric acid to a pH ~5 and sent to the electrolytic mercury cells. Figure 4 shows a simplified schematic of the portions of the process generating K071 waste from the NaOH production line.

The production process for KOH and chlorine at Plant No. 1 is identical to that described above. Figure 5 is a simplified schematic of the KOH production process. The following differences exist with respect to operations that generate the K071 waste:

- Potassium chloride (KCl) of typically 99.5+ percent purity is used as a feedstock in place of rock salt. As the potassium chloride is of higher purity, minimal saturator insolubles are generated in the KOH brine preparation circuit. The processing equipment and process conditions, however, are identical to those described above for the NaOH brine preparation system.

- Solids formed during the KCl brine purification steps are more difficult to dewater. As a result, the clarifier underflow going to the K071 sludge ponds contains a lower percentage of solids, which settle more slowly. The reason for this problem stems

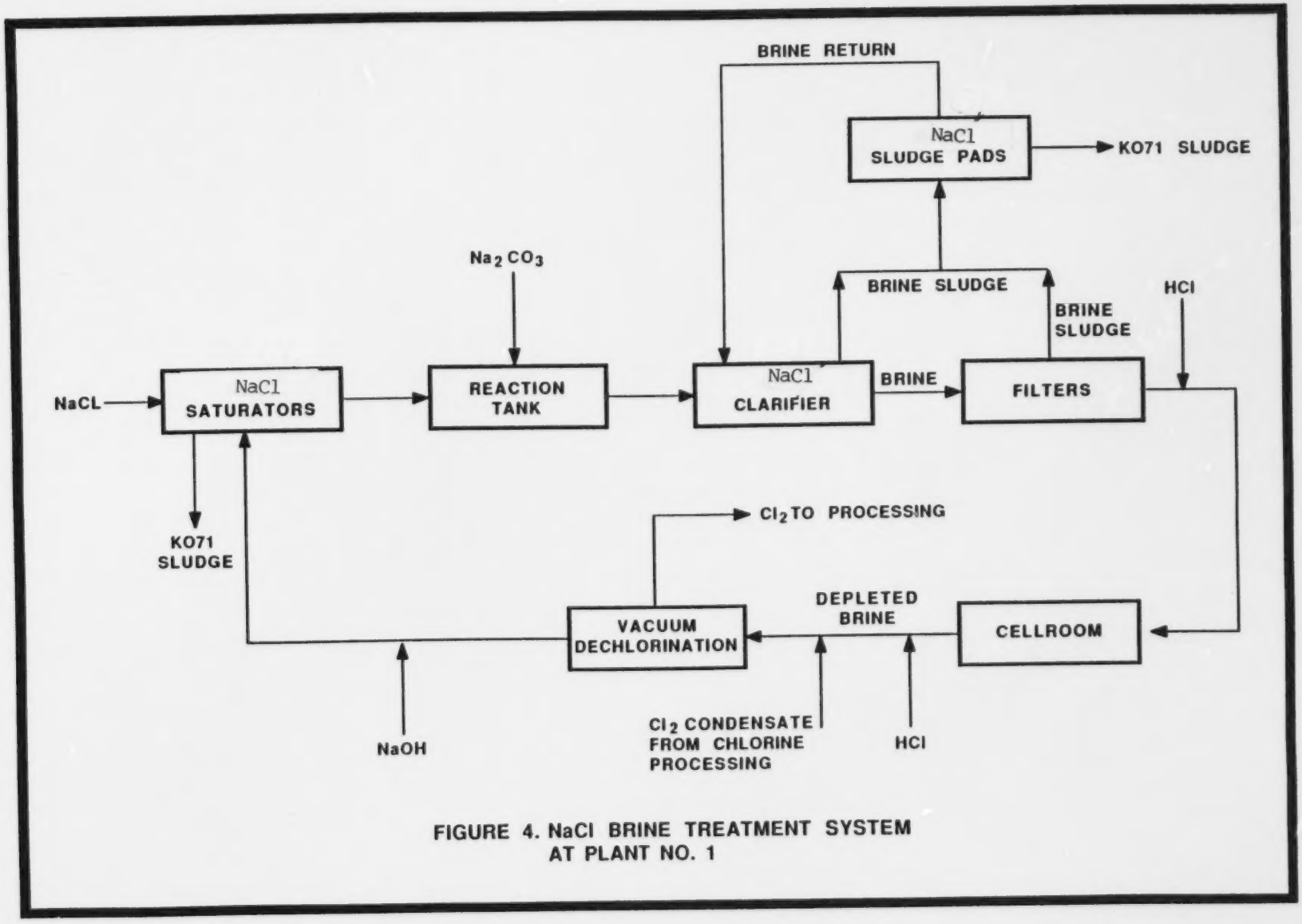

FIGURE 4. NaCl BRINE TREATMENT SYSTEM
AT PLANT NO. 1

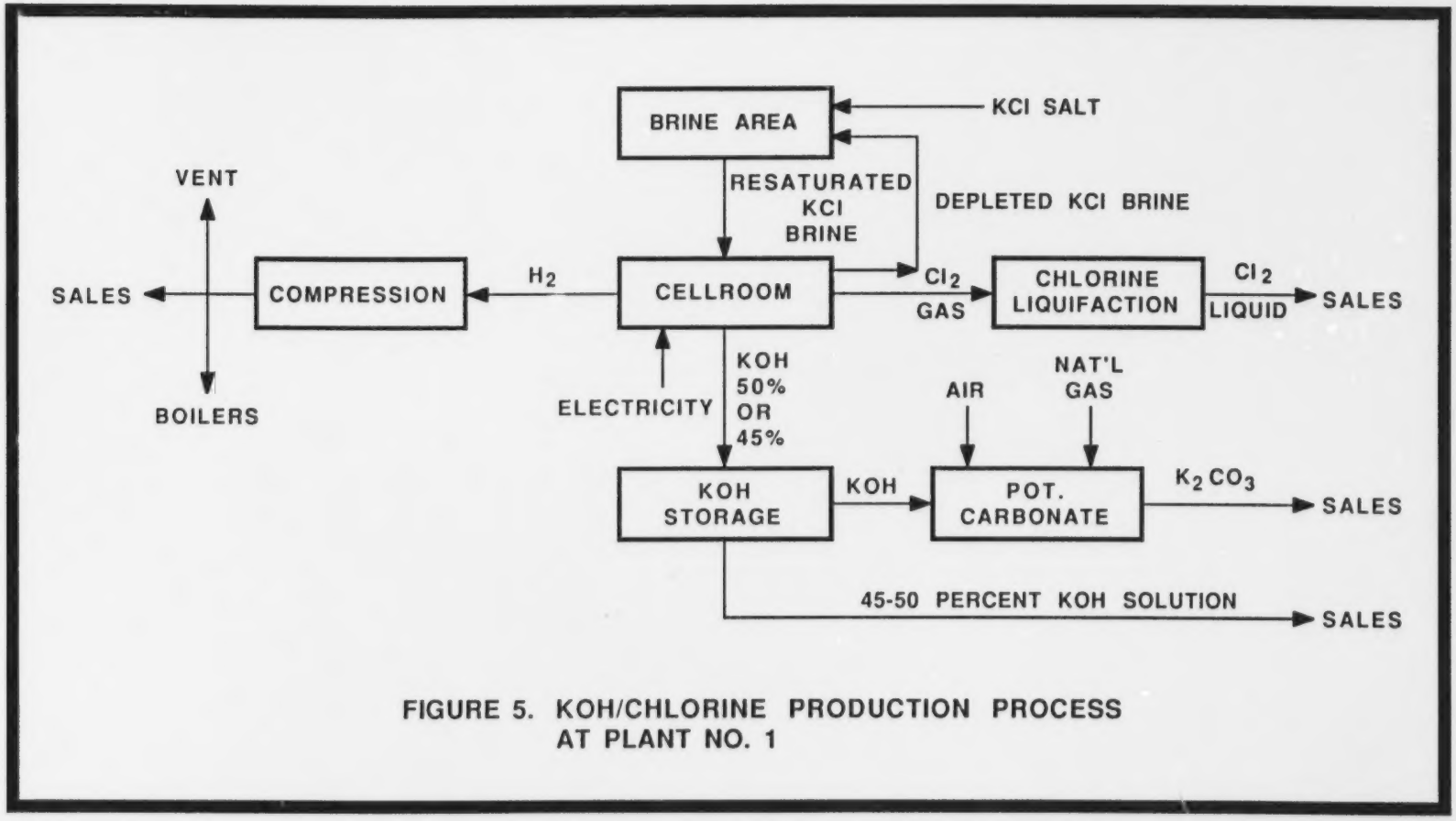

FIGURE 5. KOH/CHLORINE PRODUCTION PROCESS AT PLANT NO. 1

from the presence of traces of amine anti-caking additives present in the potassium chloride feedstock. The amines act like flotation agents and retard settling of the precipitated materials. The plant is investigating alternative sources of KCl feedstock that do not contain traces of amines.

- In the KCl brine purification step, potassium carbonate and KOH are added in place of soda ash and NaOH.

Figure 6 is a simplified schematic of the KCl brine treatment system.

Waste Stream Description

There are two sources of listed K071 waste in Plant No. 1: (1) mercury-contaminated saturator insolubles and (2) brine muds from the brine treatment purification portion of the process.

At Plant No. 1 both the KOH and NaOH production lines generate these waste streams as follows:

a) Brine saturator insolubles from the NaOH production process consist of a complex gypsum/sodium sulfate insoluble salt, undissolved sodium chloride, silica, and other insoluble materials present in the raw rock salt. The mercury compound level in this K071 waste is about 10 ppm (as mercury). About 2,500 tons per year of sodium chloride brine saturator insolubles are generated by the NaOH process train.

b) Brine purification muds from the NaOH production process (including brine clarifier underflow and brine filter backwash) consist mostly of calcium carbonate, undissolved sodium chloride, small quantities of gypsum, other insolubles, and water. Mercury levels in these K071 wastes are in the 20 to 40 ppm range. About 1,000 to 1,500 tons per year of brine purification muds are generated by the NaOH process train.

c) The KOH production process generates essentially negligible quantities of saturator insolubles because of the very high purity of the potassium chloride feedstock and the processing done by its manufacturer to remove insoluble materials. Purification of the potassium chloride brine yields sludge containing calcium carbonate, magnesium hydroxide, undissolved potassium chloride, traces of other insolubles, and water. Mercury levels in this K071 waste are about 15 to 25 ppm. This waste is more difficult to dewater than the two K071 wastes generated by the process train (as discussed above under description of the KOH manufacturing process). Up to 1,000 tons per year of K071 waste is generated from the KOH process train.

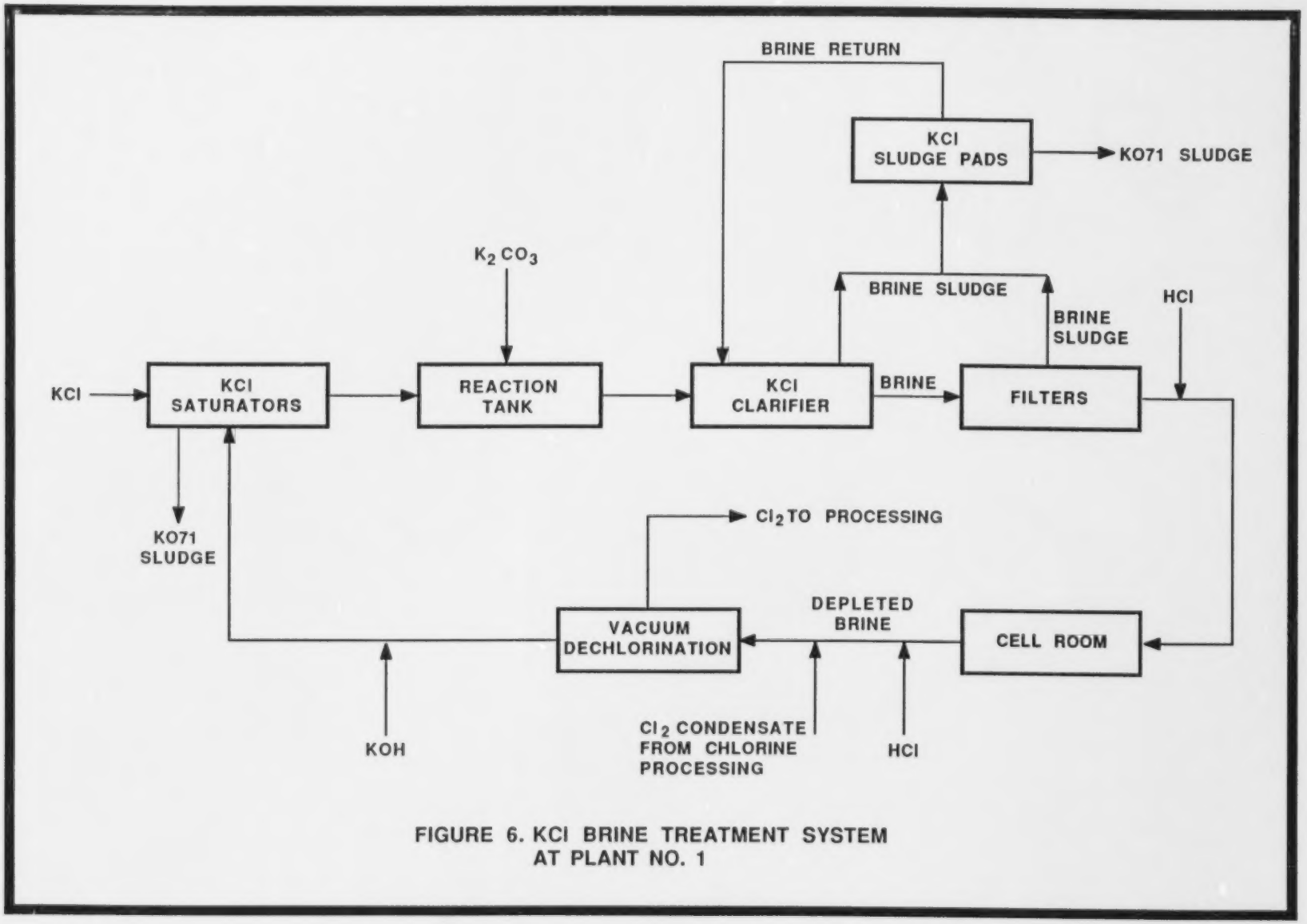

FIGURE 6. KCl BRINE TREATMENT SYSTEM AT PLANT NO. 1

Table 9 presents typical analyses of the NaCl brine-related wastes.

Current Waste Management Profile

At Plant No. 1, the K071 wastes are currently managed as follows:

- Saturator insolubles (dry solids) from the NaCl brine treatment system are periodically removed mechanically from the dissolvers and combined with the settled brine muds in the K071 sludge-holding basins prior to disposal. Blending of these two wastes enables a "dry" solid material to be loaded into roll-off bins for shipment to the hazardous waste landfill.

- Clarifier brine mud/filter backwash from each of the NaCl and KCl brine treatment systems is discharged to separate concrete-lined sludge-holding basins, where the solids settle and the liquid phases are decanted and recycled to the brine treatment systems. Separate mud-holding basins are used for the sodium and KOH production lines. In general, the muds from the KOH production lines require longer settling times. This is because the potassium chloride used contains traces of amine anti-caking agents applied to the KCl particles during production of this material in order to prevent caking during storage and shipment. Trace levels of such agents make the settling process more time consuming, and result in the KCl treatment muds having a higher water and salt content.

  After settling, blending, and air-drying, the muds are retrieved from the holding basins, containerized, and shipped to a hazardous waste landfill for final disposal.

Postulated Waste Minimization Options and Preliminary Analysis of Their Technical and Economic Feasibility

As a result of initial discussions held with plant personnel at Plant No. 1 during both the pre-audit and audit visits and subsequent evaluations by the audit team, waste minimization (WM) options for reducing or eliminating the generation of K071 waste were developed under the approved EPA hierarchy: source reduction options being more desirable and recycle/reuse options less desirable. Treatment options for the Plant No. 1 hazardous wastes, although not considered waste minimization approaches,[1] were viewed as alternatives because of

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1 The RCRA legal definition includes treatment as a WM approach. In the context of this EPA program, however, the much preferred WM approaches are source reduction and recycle/reuse, with the treatment approach used only if neither of the former approaches is available.

Table 9. Typical Analyses of K071 Wastes at Plant No. 1

Component	Weight percent
NaCl Dissolver Sludge	
$CaSO_4$	34
Na_2SO_4	34
NaCl	25
H_2O	5
Insolubles	1
Balance (Al, Mg, Fe)	<1
Hg, total	<10 ppm
Hg, EP-Tox	25 ppb
NaCl Clarifier/Filter Backwash Sludge	
$CaCo_3$	37
NaCl	35
H_2O	25
$Na_2/CaSO_4$	1
Insolubles	1
Balance (Al, Mg, Fe)	<1
Hg, total	30 ppm
Hg, EP-Tox	65 ppb
NaCl Clarifier/Filter Backwash Sludge	
$CaCO_3$	10
KCl	47
H_2O	40
$K_2/CaSO_4$	<0.5
Insolubles	1
Balance (Al, Mg, Fe)	2
Hg, total	15 ppm
Hg, EP-Tox	100 ppb

Source: Plant No. 1 in-house data.

their potential technical and economic feasibility for detoxifying the K071 waste, i.e., reduce mercury levels to <12 ppb and/or demonstrated ability to meet EPA delisting requirements at other mercury cell chloralkali facilities. The options considered under the various categories are presented below. In these presentations, preliminary economics based on order-of-magnitude cost estimates (±50 percent accuracy) are included in order to indicate the economic viability of the respective options.

Source Reduction Options

The following source reduction options have been identified for the K071 waste stream:

(A) Use of depleted brine side stream treatment for reduction of NaCl saturator insolubles generation;

(B) Use of prepurified salt as a feedstock in place of the rock salt currently used in NaOH production;

(C) Use of solar salt as a feedstock rather than the higher impurities-containing rock salt currently used;

(D) Removal of mercury from the depleted brine prior to brine resaturation and purification; and

(E) Conversion of the electrolytic mercury cells to electrolytic membrane cells, thus eliminating the generation of both K071 and K106 wastes.

These options are discussed in sufficient detail below to permit a preliminary assessment of their technical and economic feasibility.

(A) Use of depleted Brine Side Stream Treatment for Reduction of NaCl Saturator Insolubles Generation.

One of the operational problems at Plant No. 1 related to K071 waste generation is the formation of rock-like masses of insoluble materials that build up in the cone bottom section of the NaCl saturators during the rock salt dissolution operation in these units. As a result of the solids buildup, periodic shutdown of these saturators is required (every 5 to 6 weeks) in order to allow operators to enter the saturator unit taken offline and remove the rock-hard saturator insolubles material using jackhammers. This is a labor-intensive process and costs Plant No. 1 approximately $250,000 per year. Table 9 data indicate that the bulk of this material (about 70 percent by weight) is a mixture of equal

parts of sodium and calcium sulfates. This material is theorized by Plant No. 1 personnel to be the double salt $Na_2SO_4 \cdot CaSO_4$ (also known as the mineral Glauberite). If the sulfate content of the depleted brine entering the saturator can be significantly reduced below saturation level, allowing some sulfate in the incoming salt to dissolve, this could reduce or avoid the precipitation of the sodium/calcium sulfate "double salt." With a dissolved sulfate level of 36,000 ppm in the Plant No. 1 depleted brine, it is proposed to treat a side stream of 5 percent of the depleted brine flow following dechlorination and pH adjustment (approximately 150 gpm), using calcium chloride as the precipitant to remove sulfate as insoluble calcium sulfate. Following this treatment step (which would require a reactor and clarifier), the treated side stream, now low in dissolved sulfate (assumed to be 1,500 ppm), would be recombined with the balance of the depleted brine to achieve an average of approximately 34,000 ppm dissolved sulfate entering the saturator. In this manner, up to 2,000 ppm equivalent of the incoming sulfate in the raw salt, e.g., from its calcium sulfate content, can dissolve, reestablishing the saturated sulfate level, and correspondingly reducing or eliminating the potential for "double salt" formation and precipitation in the saturators.

With respect to the operating cost of this side stream operation, the single biggest cost would be that for the calcium chloride precipitant. Calculations indicate that the annual cost of this material (based on $175/ton at the plant) would be far in excess of the savings resulting from elimination of the need for an intensive labor operation to remove built-up deposits in the saturators, i.e., $58,000,000 for calcium chloride versus a $250,000 labor cost for the present saturator cleanout operation. This option is obviously not economically feasible. Use of a much cheaper sulfate precipitant, e.g., lime kiln dust, would require a far larger side stream treatment system because of the limited solubility of the latter material. Both precipitants would result in the generation of large volumes of mercury-contaminated sludges, actually increasing the amount of K071 to be disposed of, even though the dissolver solids problem would be considerably mitigated.

(B) Use of Prepurified Salt Feedstock to the Sodium Hydroxide Production Facility

One way to avoid generation of K071 wastes in the NaOH production line is to separately prepurify the salt feedstock used, i.e., substitute an essentially pure NaCl feedstock for the present rock salt material, which now requires a brine purification step (with its resultant generation of the mercury-contaminated K071 waste). The raw NaCl feedstock (rock salt) would be dissolved in water to prepare a saturated brine. The brine would then be filtered to remove insolubles and treated

to precipitate out calcium and magnesium ions as well as other trace impurities. Precipitated materials would be removed by clarification and filtration, and the purified brine would then be evaporated to recover a solid pure sodium chloride, which would then be used as a feed for the mercury cell process. With a pure salt feed, there would be minimal need for in-process purification of this material and thus minimization of the generation of mercury-contaminated brine purification wastes.[1]

The major cost associated with this option would be for evaporation of the purified brine. According to plant data, 1.72 tons of salt would have to be purified per ton of chlorine produced. As saturated brine contains 25 percent salt and 75 percent water, about 5.16 tons of water would have to be evaporated per ton of chlorine generated. Discussion with a prime vendor of commercial evaporation equipment, indicates that the use of a quadruple-effect evaporator (with suitable preheat) coupled to a centrifuge would produce a crystallized salt product and require approximately 70,000 lb/hr of saturated steam for this purpose.[2] Using a cost of $3 per 1,000 lb of 15 psig steam generated in onsite facilities, an annual cost of approximately $1.7 million would be required for steam usage. In addition, there are other direct and indirect operating costs including labor, supervision, electricity, maintenance, and depreciation on plant equipment, which would also contribute significant costs. The facility is currently spending about $150 per ton to dispose of about 5,000 tons per year of K071 waste at a commercial hazardous waste landfill. Thus, current annual disposal costs are about $750,000. In addition, a labor cost of about $250,000 is incurred annually to remove the caked rock salt impurities from the salt dissolver units. Thus, a total amount of approximately $1 million is available to offset costs of at least $2 million annually incurred by the use of a salt prepurification step. This approach is thus not

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1 Small amounts of impurities remaining after salt purification would still result in small but measurable quantities of brine purification muds, i.e., 1 to 2 tons per year.

2 Personal Communication, Mr. Frank Bella, Swenson Process Equipment, Inc., Harvey, Illinois, May 20, 1987.

economically viable.[1] It should be noted that a source of waste heat that could generate low pressure steam (though not presently available) could change these economics substantially, i.e., lower the cost of pre-purifying the salt feedstock.

(C) Use of Solar Salt as Feedstock to the Sodium Hydroxide Production Facility

Another alternative to the use of rock salt for NaOH production would be the use of solar salt, which is 99.7 percent NaCl with the balance being soluble calcium and magnesium salts (as compared to the present rock salt feedstock with 98.5 percent NaCl and a significant amount of insoluble material). Use of solar salt would eliminate the largest source of K071 waste (the saturator insolubles), but would still generate comparable quantities of brine muds - primarily magnesium and calcium hydroxides with accompanying entrained mercury - as are generated in KCl brine purification, i.e., approximately 1,000 tons per year. In addition, the cost of solar salt is $28.70 per ton FOB Bahamas, and adding an estimated freight cost of $15 per ton would make this material uneconomical to use as prepurified salt (current rock salt cost at the plant is under $15 per ton).

(D) Removal of Mercury from Depleted Brine Leaving the Mercury Cells

Two proposed in-process modifications for removal of entrained mercury from the depleted brine leaving the mercury cells, were discussed with plant personnel during the audit visit. Either of these, if technically and economically viable, could reduce or eliminate the generation of K071 waste. These two options are discussed below:

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1 In this regard, one audit team suggestion was considered, whereby Plant No. 1 would interest a sufficient number of mercury cell chloralkali plants in pooling their salt purchasing volume with a rock salt producer in a cooperative effort to have the producer prepurify the rock salt for distribution to this group. This group of chloralkali plants could jointly defray the cost of the new rock salt purification equipment at the rock salt production site in return for long-term contractual commitments for the prepurified salt. One significant problem with this suggestion is the fact that there is an insufficient number of mercury cell plants within a reasonable distance of a rock salt producer that could benefit from this approach. Of the 14 mercury cell plants that could potentially benefit from access to prepurified rock salt, only one or two in any given salt producing region would be able to benefit from this arrangement.

(1) The first of these options would involve treatment of depleted brine from the mercury cells with sodium sulfide (Na_2S) to precipitate essentially insoluble mercuric sulfide before the depleted brine is returned to the brine resaturation and treatment portion of the process. The plant had previously investigated the possibility of removing entrained mercury from the depleted brine when an experiment was carried out to test operation of a membrane electrolytic cell at the site. The need existed to produce a mercury-free brine to be used as feed to this cell, and sodium hydrosulfide (NaSH) was used to precipitate mercury as the insoluble sulfide. The plant was able to produce a mercury-free brine using this procedure. Adaptation of this procedure as a commercial process for removal of mercury from the depleted brine prior to the brine resaturation step was explored for its potential as a viable source reduction option. Two possible approaches under this option include the following:

(a) Disposal of the mercuric sulfide waste generated by the sulfide precipitation step. In this approach, the depleted brine from the mercury cells following dechlorination and pH adjustment with NaOH solution to a pH of 7 to 8, would be treated in a number of parallel in-line static mixers with sodium sulfide (Na_2S) to precipitate mercury as insoluble mercuric sulfide (this reaction is complete within 30 to 60 seconds). Enough Na_2S is added to ensure complete precipitation of the mercury and reaction with the residual chlorine in the dechlorinated brine.[1] The resulting slurry would then be fed to a hold tank where filter aid (diatomaceous earth) and coagulant (if required) are added, and the mixture is then fed to pressure leaf filters. The filtered brine now free of entrained mercury would then be fed to the salt dissolvers, and the brine treatment and purification process would now generate a non-hazardous waste, which could be placed in a sanitary landfill after appropriate delisting.

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1 With an average of 70 ppm of residual Cl_2 in the depleted brine after dechlorination reacting to form hypochlorite ions (OCl^-) in the brine, the $(OCl)^-$ is expected to react with sodium sulfide to form NaCl and Na_2SO_4. In the latter reaction (at an alkaline pH), one mol of Na_2S would be consumed in reacting with 4 mols of NaOCl. Together with the reaction of Na_2S with soluble mercury (assumed to be present as mercuric chloride) in the depleted brine, a total of 151 tons per year of Na_2S (as 100 percent material) would be required at an approximate delivered cost of $500/ton or $75,000/year.

Approximately 240 lb/day of mercury would be removed from the depleted brine as mercuric sulfide. This material would be included in a 50 percent solids filter cake (the recovered form of this waste) of approximately 24,000 lb/day (12 tons/day), based on data on K106 waste generation in mercury cell plants using sulfide treatment for collected wastewaters. With mercury valued at about $6/lb (equivalent to $518,000/yr replacement cost), treatment costs including labor, chemicals (Na_2S), power, and maintenance are estimated to be approximately $250,000/yr, and a disposal cost of roughly 4,300 tons per year of this waste at the currently used hazardous waste landfill of about $645,000/yr, the total annual cost for treating and disposing of this waste would be approximately $1.4 million per year. This is over double the present cost of K071 waste disposal from the NaOH production facility ($0.6 million per year), and the option would therefore not be economically viable.

(b) Recovery of mercury from the mercuric sulfide waste generated by the sulfide precipitation step. A retort of the multiple hearth furnace type is commercially available to recover the mercury from the mercuric sulfide sludge, and would cost approximately $1.0 million to install based on the capacity and feed rate required. The 12 tons per day of mercuric sulfide filter cake generated in the sulfide precipitation step (having been washed free of residual NaCl in the filtration step) would be continuously fed to the retort, the mercury vapor condensed, and the recovered mercury recycled to the electrolytic cells.[1] The retorted residue, consisting of about 6 tons per day of essentially pure filter aid with traces of iron sulfide, would be recycled to the sulfide filtering step, with a small amount of this material (assumed to be 10 percent or approximately 0.6 ton per day) disposed of as a delisted non-hazardous waste to a local sanitary landfill.[2]

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1 It is assumed that the mercuric sulfide in the retort would vaporize at 1000°F, and, in the presence of air swept through the retort, would react to form metallic mercury and SO_2. After the mercury is condensed, a caustic scrubber would be used to remove the SO_2 from the residual vent gas. Appropriate monitoring of the vent gases would be required for residual mercury and SO_2 emissions.

2 Based on preliminary Plant No. 1 test data, EP-tox leachable mercury from this residue should be less than 12 ppb (assumed to be the EPA delisting level for this waste).

The operating cost of retorting for mercury recovery (assuming a natural gas-fired retort) is estimated as $100 per ton of dry feed to the retort.[1] These costs include labor, natural gas, electricity, and maintenance (with the latter assumed to be 60 percent of the total operating cost) and total $216,000 per year. Other direct operating costs (including labor, Na_2S, power, and maintenance) for the mercuric sulfide precipitation step are estimated as $250,000 per year. Total direct operating cost is therefore $358,000 per year. The total installed cost of the mixer/filter/retort system for mercury precipitation and recovery is estimated at $1.4 million. The savings in disposal cost for K071 based on disposal of the delisted mercury-free saturator insolubles and brine muds and mercury retort residue in a nearby approved sanitary landfill would be $397,000 annually.[2] Since the total operating costs for this option exceed the savings in landfill costs, there is no payback available with this option, and it is not economically viable.[3]

(2) A second possible in-process modification discussed with plant personnel involves the use of ion exchange resin for dissolved mercury removal from depleted brine leaving the mercury cells. The significant problems with this approach include the following:

- the lack of a commercially available resin capable of treating a depleted brine containing significant levels of residual chlorine (even after dechlorination) without extensive pretreatment to remove the chlorine;

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1 This number represents three times the operating cost estimate developed in 1974 for operation of a similar retort used for this purpose (EPA 660/2-74-086, p.72). Plant No. 1 onstream time is assumed to be 360 days per year for all operating cost estimates in this report.

2 Disposal cost in a lined sanitary landfill within approximately 30 miles from Plant No. 1 would cost about $33/ton. This cost has been used throughout the report as that for disposal of delisted K071 waste in an approved sanitary landfill. "Approved" in this context is taken to mean that the landfill is equipped with a clay or synthetic liner with a permeability of less than 10^{-7} cm/sec.

3 Payback period is defined in this report as the total incremental investment for the option considered divided by the net savings in annual direct operating costs. In this case, the payback is (1,400,000/397,000 - 216,000 - 250,000) or -20 years.

- the relatively low flow rates available for use with present commercial resins (10 to 15 bed volumes/hr) requiring very large resin beds; and

- the relatively low mercury adsorption capacity for commercially available resins before breakthrough occurs (≈0.7 percent by weight of available capacity for commercial resins evaluated by Plant No. 1).

This approach thus appears to be both technically and economically nonviable.

(E) Conversion of the Mercury Electrolytic Cells to Membrane Electrolytic Cells, Thus Eliminating the Generation of Both K071 and K106 Wastes[1]

The use of membrane technology in chloralkali plants has become firmly established, with a total of 12,000 metric tons of caustic production per day or approximately 11 percent of worldwide capacity using this technology in 1987.[2] Although membrane cell technology appears to be the brine electrolytic cell technology of choice for new installations worldwide, only about 3 percent of chloralkali capacity in the U.S. currently uses this process, primarily because of the lack of growth in the domestic chloralkali industry.[2] With no new mercury cell chloralkali plants planned and the existing mercury cell plants in the U.S. for the most part nearing the end of their useful lives, either replacement of this capacity with membrane technology or conversion of the existing mercury cells to membrane cells is becoming a distinct possibility. An additional incentive for replacement of mercury cells with membrane cells would be elimination of the generation of K071 and K106 wastes. A source reduction option was evaluated wherein the existing mercury cell facility at Plant No. 1 was replaced with membrane cells incorporating Dupont Nafion perfluorinated membranes.[3]

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1 Information in this section is derived from a paper by M. Esayian and J.H. Austin (Esayian, M. and Austin J.H. 1984).

2 Personal Communication, Mr. David Peet, E.I. Dupont de Nemours and Co., Inc., Wilmington, Delaware, July 22, 1987.

3 This does not imply any EPA endorsement of this product.

In addition to electrolyzer conversion, a mercury cell to membrane cell retrofit, based on present technology, is assumed to require three major changes in auxiliary facilities:

- The use of ion exchange resin in a new secondary brine purification step to remove dissolved calcium and magnesium to a level of less than 50 ppb. At least two resin beds are required, one bed being online while the other is being regenerated. This step is well established technology.

- Evaporation to concentrate the 32 to 35 percent NaOH or KOH from the membrane process to the 50 percent product required. This is assumed to require additional steam generating capacity.

- A caustic recirculation loop to provide temperature control as well as mixing in order to achieve a uniform concentration profile in the cathode chamber. Deionized water is added to the catholyte loop to control the NaOH or KOH concentration.

The existing brine loop can be used in the mercury cell conversion, although the higher salt conversion capability of the membrane cell process will significantly reduce the brine hydraulic flow. Selection of the proper membrane electrolyzer designs should minimize cell room changes. It is assumed that the present rectifiers and current conductors at the Plant No. 1 cell room will not require major changes. Figure 7 is a simplified schematic of the revised chloralkali process employing membrane cell technology at Plant No. 1. While shown for the NaOH manufacturing portion of the plant, this schematic would apply to both NaOH and KOH production facilities.

Based on the process shown in Figure 7, the investment for membrane conversion at Plant No. 1 is estimated as $61,000/ton/day of 100 percent NaOH (or KOH)[1]. With combined NaOH and KOH production (100 percent basis) of 307 tons per day, the total investment for the membrane conversion is $19.0 million. An estimate of direct annual operating cost was developed based on the following assumptions:

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1 Personal Communication, Mr. David Peet, E. I. DuPont deNemours and Co., Inc., Wilmington, Delaware, July 22, 1987. This is an estimate based on a generic plant design that is believed to be of sufficient accuracy i.e., well within the ±50 percent accuracy used for estimates in this report, for this preliminary estimate.

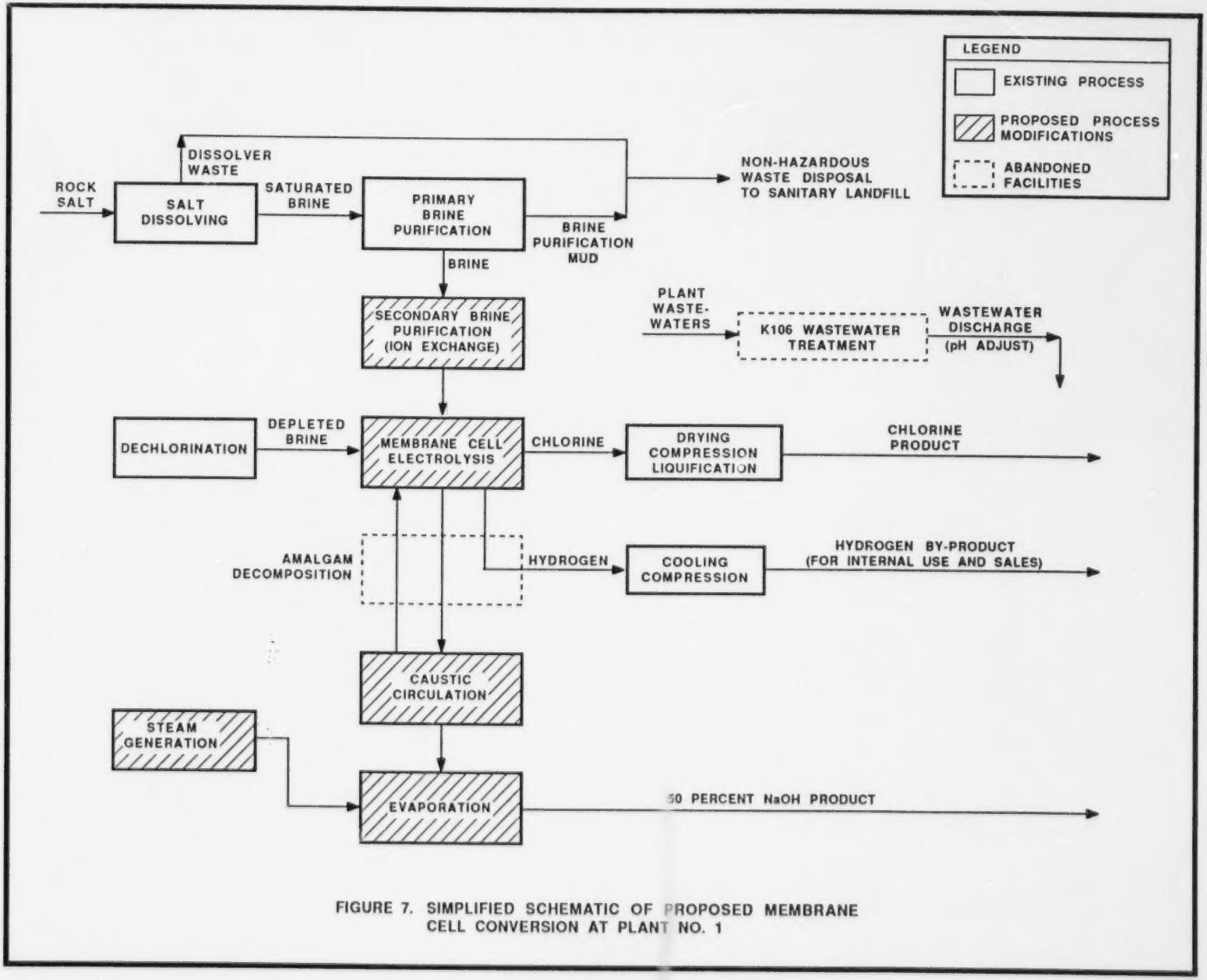

FIGURE 7. SIMPLIFIED SCHEMATIC OF PROPOSED MEMBRANE CELL CONVERSION AT PLANT NO. 1

- Electric power configuration:
  - Mercury cell: 2,950 KWH/metric ton of 100 percent NaOH (or KOH)
  - Membrane cell: 2,200 KWH/metric ton of 100 percent NaOH (or KOH)[1]
- Electric power cost: 4.9 cents/KWH
- Steam cost: $4.80/1,000 lb
- Membrane life: 2 years
- Auxiliary power consumption: 260 KWH/metric ton of 100 percent NaOH (or KOH)
- Steam for evaporation: 200 lb/metric ton of 100 percent NaOH (or KOH)

Operating costs shown are in 1985 dollars and are assumed to be applicable in 1987 dollars.

The difference in direct operating costs resulting from electric power and steam costs (in the mercury cell case) and electric power, steam, membrane replacement, and miscellaneous costs (in the membrane cell case) is estimated as $9.4 million/year. Other direct operating costs are assumed to be the same for both cases. With respect to waste disposal, the difference between K071 and K106 hazardous waste disposal of approximately 5,000 tons per year (in the mercury cell case) and disposing of this material in the non-hazardous form (in the membrane cell case) is about $600,000 per year. With a total savings of about $10.0 million per year in direct operating costs, the payback period is (19.0 million/10.0 million) or 1.9 years, making the membrane conversion economically attractive based on these numbers.

Space requirements for the additional equipment (including one common stream generating system, two sets of evaporators for the NaOH and KOH products, and two ion exchange systems for secondary brine purification), are believed to be adequate for the required plant revamp at Plant No. 1 if this option were to be adopted.

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[1] Current efficiency for KOH production in membrane cell electrolyzers is higher than for NaOH. The figure shown is for NaOH, so that this is a conservative assumption.

Recycle/Reuse Options

There were no recycle/reuse options available for recovery of the very small daily amount of mercury entrained in the K071 waste (<5 lb/day). This amount of mercury (primarily in the ionic form) is dispersed in approximately 30,000 lb/day of brine purification muds and saturator insolubles.

Treatment Options

While treatment is not a WM option, it is possible that with only one technically and economically viable source reduction option deemed by the audit team to be potentially available to Plant No. 1 (replacement of the mercury cell system with membrane cells and appropriate auxiliary equipment), consideration should be given to technically and economically feasible treatment alternatives to the present disposal method at Plant No. 1 for the K071 waste.[1] Such treatment, if it would render the waste non-hazardous, would permit disposal of the treated material in a sanitary landfill once the waste was suitably delisted. In this regard, the August 1988 ban on disposal of these RCRA listed wastes (K071 and K106) in hazardous waste landfills, lends additional impetus to consideration by Plant No. 1 of a treatment alternative to the present method of disposal.[2] Three proposed treatment options were considered:

(1) Use of a washing process to render the NaCl saturator insolubles portion of the K071 waste non-hazardous. The waste would be considered non-hazardous by EPA because of the reduction of EP-tox leachable mercury level to <12 ppb.[3] No separate treatment is planned for the KCl saturator insolubles, since this waste is negligible in quantity.

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1 It should be noted that the audit team had no knowledge of the investment priorities at Plant No. 1 and thus could not judge whether or not the proposed source reduction option (which would involve an investment of approximately $20 million) would be given serious consideration at this time.

2 In addition to this impetus, BDAT (best demonstrated available technology) requirements, when promulgated by EPA for listed wastes K071 and K106, will require mercury cell chloralkali plants presently disposing of these wastes in hazardous waste landfills, to meet much more stringent mercury levels in order to continue disposal in landfills.

3 The current maximum level in the EP-tox leachate required for delisting of the K071 waste by EPA at the waste generation level in Plant No. 1 is 12 ppb of mercury.

(2) Use of a washing process for the NaCl saturator insolubles combined with an experimental chemical treatment process developed by Plant No. 1 for the brine clarifier mud/filter backwash solids/hot process treatment solids. The combined treatment would render the total K071 waste non-hazardous by reducing the EP-tox leachable mercury level in this waste to <12 ppb. The Plant No. 1 experimental process would be used on both the NaCl brine treatment waste and (separately) on the KCl brine waste. In the latter case, only the brine purification muds and filter backwash solids would be treated by the Plant No. 1 experimental process.

(3) Use of a washing process to treat the NaCl saturator insolubles portion of the K071 waste and a technique used in the Vulcan Treatment Process to chemically treat the brine clarifier muds/filter backwash solids/hot process treatment solids portion of the NaCl brine-based K071 waste.[1] Separate use of the Vulcan treatment technique would be employed for the KCl brine-based K071 waste. These procedures would render the entire K071 waste non-hazardous by reducing the EP-tox leachable mercury level in this waste to <12 ppb.[2]

It is to be noted that option (1) above is common to all three proposed treatment options. Plant No. 1 could install option (1) initially and add either option (2) or (3) at a later date (but before the August 1988 RCRA ban on landfilling these wastes), when delisting of the NaCl saturator insolubles is achieved and small-scale trials of either option (2) or (3), together with detailed economic studies of these approaches, enables Plant No. 1 to make an appropriate choice of a treatment step for the brine purification muds. The three options are discussed in detail below.

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1 A K071 treatment process developed by the Vulcan Chemicals, Port Edwards, Wisconsin, chloralkali facility and available to the mercury cell chloralkali industry. This process, used by the Vulcan facility to obtain EPA delisting of their K071 waste, is currently incorporated in the plant operation.

2 As a result of adoption of option (1), (2), or (3), wastewater treatment costs in the K106 treatment operation would show a small but measurable increase caused by as much as a 10 ton per year increase in K106 generation.

Option (1) Use of a washing process to convert the NaCl saturator insolubles portion of K071 waste into a non-hazardous form.

The largest portion of K071 waste at Plant No. 1 is the NaCl saturator insolubles. This stream is approximately 50 percent (2,500 tons per year) of the total hazardous waste shipped offsite. In option (1), a water washing treatment approach was applied to this stream only. A number of mercury cell chloralkali producers have been successful in delisting all or part of the K071 waste stream, using a washing technique utilizing either water or depleted brine.[1]

It is assumed that discharge of the saturator solubles from the Plant No. 1 offline NaCl saturators could be scheduled so that the proposed water washing process can be carried out on a continuous basis. This material would not be mixed with the dilute brine clarifier sludge (as is done now), but would be stored separately on the existing sludge pad as the feed point in the proposed treatment option. The brine clarifier underflow stream and (when generated) the hot process treatment tank solids discharge (see Section 2 for a description of the hot process system for NaCl brine preparation) would have to be continuously combined, clarified, thickened, filtered, and shipped offsite as hazardous waste, as is discussed below.

It is proposed to water wash the NaCl saturator insolubles material (characterized in Table 2 - NaCl Dissolver Sludge) at the rate of approximately 7 tons per day (580 lb/hr). The process would consist of loading this material from the sludge pad storage area (using a portable conveyor) into a propeller-agitated slurry tank. In the tank, fresh water makeup and a recycle dilute brine stream (derived from the residual salt in the saturator insolubles) would be used to prepare a slurry (assumed to be 25 percent solids) to be used as feed to a horizontal vacuum belt filter. Large particulate (rocks, trash, etc.) would be

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1 Stauffer Chemical Co., St. Gabriel, Louisiana, Olin Chemical Corp. Charleston, Tennessee, Vulcan Chemicals, Port Edwards, Wisconsin, and Stauffer Chemical Co., Le Moyne, Alabama. These companys' respective EPA delisting petitions contain appropriate supporting data and process information on this approach. The operating mechanism in the washing process is presumed to be a metathesis reaction, i.e., the glauberite ($Na_2SO_4 \cdot CaSO_4$) is assumed to dissolve, soluble calcium ions present would disproportionate the sodium ions, and calcium sulfate would recrystallize as either gypsum or anhydrite. Lab-scale tests at Plant No. 1 have tended to confirm this mechanism.

periodically drained from the bottom of the slurry tank and held on the sludge pad for final disposal. Slurry would be fed through a head tank to the filter where a countercurrent water-washing scheme is achieved. In this scheme, slurry is continuously delivered to the feed end of the unit and filtered solids (assumed to be a 75 percent solids cake) are discharged at the opposite end. Fresh wash water is applied to the cake near the discharge area, passes through the cake, is collected in a vacuum receiver, and is reapplied to the cake nearer the feed end of the filter in countercurrent fashion. Two to four washing stages would normally be used. Wash liquor discharge from the unit is sent to the Plant No. 2 wastewater treatment operation described in Section 3.[1] Based on extensive pilot-scale treatment of a similar saturator insolubles material, the filter cake would have 1 to 15 ppm mercury and the EP-tox leachate would have about 5 ppb mercury.[2] The filter cake, once delisted, could be disposed of in a lined sanitary landfill within about 30 miles from Plant No. 1.

A simplified schematic of the proposed treatment scheme is shown in Figure 8.

The brine clarifier underflow, filter backwash discharge, and hot process reactor tank slurry discharge, which, because of the method of operation, is quite dilute (containing less than 0.5 percent solids in the combined stream), is presently combined with the saturator insolubles discharge on the sludge pad to produce a "dry" sludge prior to shipment offsite to a hazardous waste landfill. Adoption of proposed treatment option (1) by Plant No. 1 would require that the brine wastes be handled separately prior to discharge as a final waste. This would involve discharging the combined brine clarifier underflow/filter backwash solids/hot process reactor tank solids stream to a separate clarifier-thickener in order to produce an underflow sufficiently high in solids to feed to a dewatering filter such as a rotary vacuum filter (approximately 10 to 20 percent solids in the filter feed is assumed to be achievable by this technique). The filter cake from this treatment

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1 As a result of adoption of option (1), (2), or (3), wastewater treatment and waste disposal costs in the K106 treatment operation would show a small but measurable increase because of an increase in K106 generation of up to 10 tons per year.

2 Stauffer Chemical Company, St. Gabriel, Louisiana. Delisting Petition to EPA, April 18, 1982, Table III.

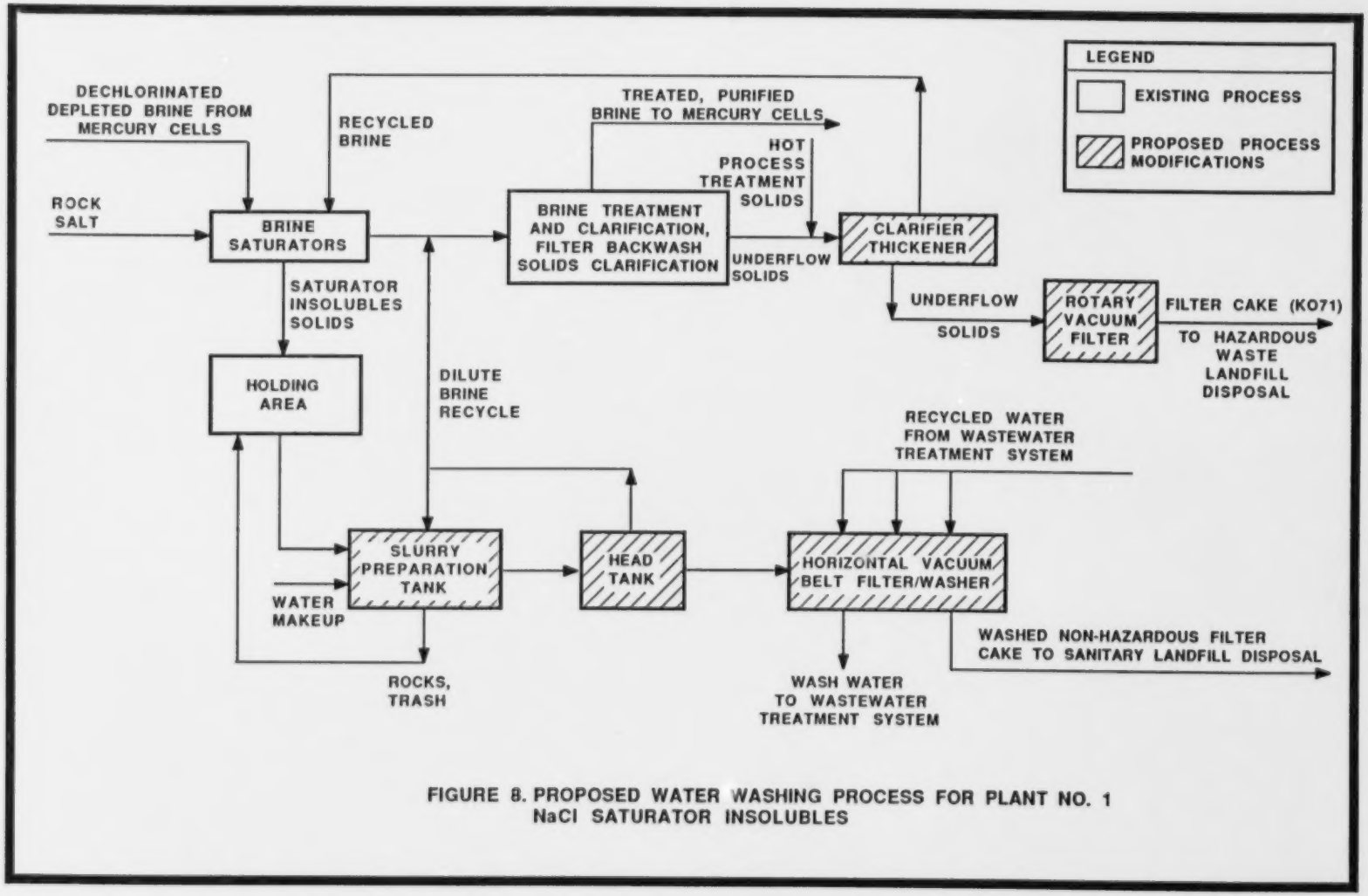

FIGURE 8. PROPOSED WATER WASHING PROCESS FOR PLANT NO. 1
NaCl SATURATOR INSOLUBLES

sequence would be discharged as K071 waste to the presently used hazardous waste landfill and the clarifier-thickener overflow and filtrate recycled to the brine circuit.[1] This treatment sequence is also incorporated in Figure 8. With respect to the costs entailed by the adoption of this proposed treatment option, the major capital cost items include the following:

- Stirred slurry tank for saturator insolubles feed preparation (1,000 gal);
- Corrosion resistant horizontal vacuum belt filter (200 sq ft filtration area) for saturator insolubles washing;
- A clarifier/thickener for the combined brine clarifier/hot process tank solids slurry (30 ft diameter x 10 ft high); and
- A corrosion-resistant rotary vacuum filter (100 sq ft filtration area).

Together with associated instrumentation, piping, and pumps, the total installed cost for the proposed saturator insolubles washing process (including separate treatment of the NaCl brine treatment wastes) is estimated to be $700,000. Annual direct operating costs (including labor, electricity, water, and maintenance) are estimated at $50,000 per year. Cost of disposal of the 2,500 tons per year delisted K071 saturator insolubles at $33/ton is estimated as $83,000 per year. Based on an assumed production rate of 800 tons per year of K071 brine mud waste (as a 75 percent solids filter cake), disposal cost in the presently used hazardous waste landfill is estimated as $120,000 per year. Net savings (over present disposal cost of $600,000 for the K071 NaCl brine purification muds and saturator insolubles) is thus $380,000 per year, with a payback period estimated as (700,000/380,000-50,000) or 2.1 years. This option thus appears worthy of further detailed examination as a means of creating a delistable waste.

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1 It is important to note that an additional benefit derived from implementing this dewatering and filtration technique (if successful) would be a major reduction in the amount of hazardous waste sent offsite to the presently used hazardous waste landfill. Instead of 1,500 tons per year of NaCl brine muds sent offsite (along with 2,500 tons per year of treated saturator insolubles wastes), a net production of about 800 tons per year of K071 brine-related waste as a 75 percent solids filter cake may be achievable. This approach will require some research and development effort to establish the appropriate operating parameters.

Consideration of the location requirements for installing the proposed option for the NaCl saturator insolubles, suggests the following as appropriate for this need:

- An area, presently vacant, believed the NaCl K107 sludge storage pads, should be available to install the slurry tank, head tank, and horizontal vacuum belt filter for the saturator insolubles water washing treatment. An area adjacent to the present NaCl brine clarifier should be suitable for installation of the new clarifier/thickener to process the combined NaCl brine clarifier underflow/filter backwash solids/hot process treatment solids stream. An existing one story building on the opposite side of the present NaCl brine clarifier, should be usable to house the required rotary vacuum dewatering filter.

Option (2) Use of a washing process for the saturator insolubles portion of K071 waste and a Plant No. 1 experimental process for the brine purification muds portion of K071 waste in order to convert these wastes into a non-hazardous form suitable for delisting.

This option proposes the use of the water washing treatment process described under treatment option (1) for the NaCl saturator insolubles, and the addition of an experimental process developed by Plant No. 1 to treat the total NaCl brine purification and stream (brine clarifier muds, filter backwash solids, and hot process treatment muds). In a separate treatment step, the Plant No. 1 experimental treatment scheme would be used to process the KCl brine purification muds (brine clarifier mud and filter backwash solids) in an identical manner. As a result of these processing steps, the entire K071 treated waste stream would show less than 12 ppb leachable mercury in the EP-tox procedure, and would be suitable for ultimate EPA delisting and disposal in a nearby approved sanitary landfill.

The experimental process developed by Plant No. 1 (as applied to the NaCl brine purification waste) involves first treating the combined NaCl brine clarifier mud/filter backwash/hot process treatment solids through the clarification/thickening sequence described under option (1) above. The underflow slurry from the clarifier/thickener would be pumped to a hold tank where filter aid is added, and the resulting slurry is then fed to a vacuum filter. The filter cake would be subjected to multiple step washing on the vacuum filter in order to remove as much residual solubilized mercury as possible. The filter cake wash steps would include the following:

- One to two washing steps using acid pH wash water to solubilize as much mercury from the filter cake as possible, with the filtrate then sent to the plant wastewater treatment system for mercury removal.

- A final wash using NaSH solution (following appropriate pH adjustment) in sufficient excess to precipitate the remaining trace amounts of solubilized mercury present in the filter cake as insoluble mercuric sulfide. NaSH solution filtrate would be recycled with periodic makeup added as required.

The discharged filter cake would be low enough in leachable mercury such that the EP-tox leachate from the material is expected to indicate less than 12 ppb mercury. Preliminary tests of this technique at Plant No. 1 indicated a mercury level in the EP-tox leachate of 2 ppb. The treated filter cake after suitable delisting would be disposed of in a nearby sanitary landfill.

A simplified schematic of this proposed option (applicable to both the NaCl and KCl K071 brine purification waste streams) is shown in Figure 9.

The capital equipment requirements for both the NaCl and KCl brine purification waste treatment schemes in option (2) are assumed to be identical, i.e., a clarifier/thickener, a NaSH storage tank, and a horizontal belt vacuum filter, together with all appropriate instrumentation, piping, and pumps. A total installed cost of $500,000 is estimated for both treatment lines ($250,000 per treatment line shown in Figure 8). Annual direct operating cost (including labor, chemicals, electricity, water, and maintenance) for both waste streams is estimated as $160,000 per year. Based on disposal of an estimated 1,500 tons per year of delisted waste filter cake from the combined NaCl and KCl K071 brine purification wastes from treatment option (2) at $33/ton at a nearby lined sanitary landfill, as compared to the present combined waste disposal costs for 2,500 tons per year at $150 per ton in the presently used hazardous waste landfill, the net savings in disposal cost is $325,000 per year and overall net savings in annual costs is $165,000.

With respect to the treatment of the NaCl saturator insolubles under option (2), the capital and operating costs are reduced, since the equipment designated in option (1) for brine treatment waste handling prior to disposal as a K071 hazardous waste is now used to produce a delistable waste from the NaCl brine-derived waste. Overall payback time for implementation of option (2) on both the NaCl and KCl production lines is (500,000 + 500,000/262,000 + 165,000) or 2.3 years. Option (2) is therefore of interest for further evaluation, in particular with respect to additional research and development needed to establish the optimum operating parameters for the NaSH treatment step.

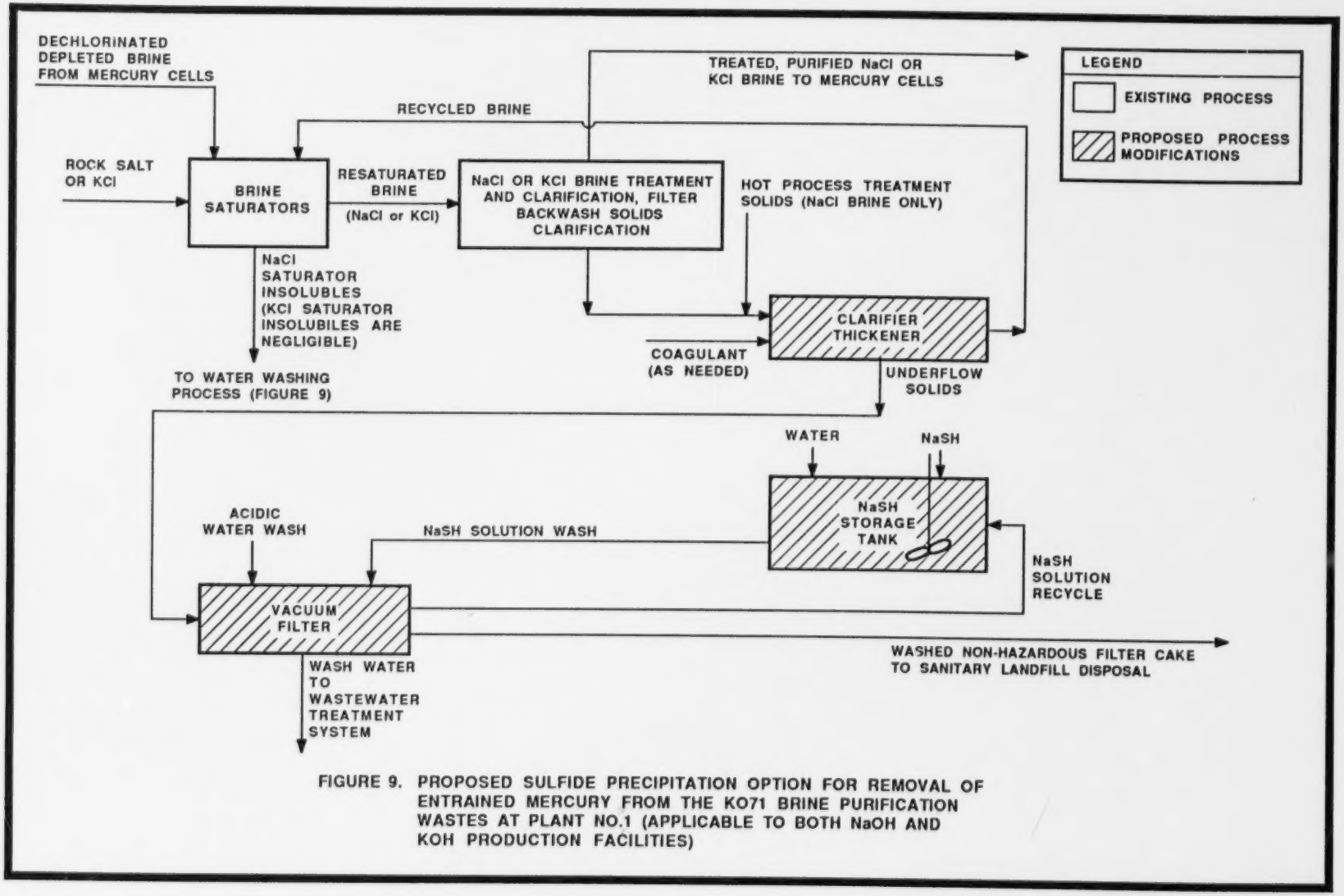
DECHLORINATED DEPLETED BRINE FROM MERCURY CELLS
TREATED, PURIFIED NaCl OR KCl BRINE TO MERCURY CELLS
LEGEND
EXISTING PROCESS
PROPOSED PROCESS MODIFICATIONS
RECYCLED BRINE
ROCK SALT OR KCl
BRINE SATURATORS
RESATURATED BRINE
(NaCl or KCl)
NaCl OR KCl BRINE TREATMENT AND CLARIFICATION, FILTER BACKWASH SOLIDS CLARIFICATION
HOT PROCESS TREATMENT SOLIDS (NaCl BRINE ONLY)
NaCl SATURATOR INSOLUBLES (KCl SATURATOR INSOLUBILES ARE NEGLIGIBLE)
TO WATER WASHING PROCESS (FIGURE 9)
CLARIFIER THICKENER
COAGULANT (AS NEEDED)
UNDERFLOW SOLIDS
WATER
NaSH
NaSH STORAGE TANK
ACIDIC WATER WASH
NaSH SOLUTION WASH
NaSH SOLUTION RECYCLE
VACUUM FILTER
WASHED NON-HAZARDOUS FILTER CAKE TO SANITARY LANDFILL DISPOSAL
WASH WATER TO WASTEWATER TREATMENT SYSTEM

FIGURE 9. PROPOSED SULFIDE PRECIPITATION OPTION FOR REMOVAL OF ENTRAINED MERCURY FROM THE KO71 BRINE PURIFICATION WASTES AT PLANT NO.1 (APPLICABLE TO BOTH NaOH AND KOH PRODUCTION FACILITIES)

Consideration of the location requirements for installation of the proposed treatment option for the NaCl saturator insolubles and both the NaCl and KCl brine treatment/wastes, suggests the following areas as appropriate for these needs:

- An area, presently vacant, believed the NaCl K107 sludge storage pads, should be available to install the slurry tank, head tank, and horizontal vacuum belt filter for the saturator insolubles water washing treatment. An area adjacent to the present NaCl brine clarifier should be suitable for installation of the new clarifier/thickener and NaSH storage tank to process the combined NaCl brine clarifier underflow/filter backwash solids/not process treatment solids stream. An existing one story building on the opposite side of the present NaCl brine clarifier should be usable to house the required washing/dewatering vacuum filter.

- An area behind the KCl brine sludge pads and near the wastewater storage tankage, should be available for the installation of the new clarifier/thickener, NaSH storage tank, and the washing/dewatering vacuum filter to process the combined KCl brine clarifier underflow/filter backwash solids. A one story structure would need to be built to house the filter operations.

Option (3) Use of a washing process for the NaCl saturator insoluble portion of K071 waste and employment of a technique used in the Vulcan Treatment Process to chemically treat the NaCl brine clarifier muds/filter backwash solids/hot process treatment solids portion of the K071 waste as well as the KCl-derived brine purification waste.

This option proposes the use of the water washing process described under treatment option (1) for the NaCl saturator insolubles, and the addition of a portion of a commercially available K071 waste treatment process (developed by Vulcan Chemicals at their Port Edwards, Wisconsin, chloralkali facility), in order to treat the brine purification wastes from both the NaCl and KCl brine production areas. The Vulcan process involves the use of pH adjustment[1] and hypochlorite treatment on the

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1 Sulfuric acid is used in adjustment of pH to the 2.5 to 3.0 range. This procedure promotes growth of gypsum crystals, which ensures minimal entrainment of solubilized mercury in the later filtration/washing step.

combined NaCl brine clarifier mud/filter backwash solids/hot process treatment solids (or the combined KCl brine clarifier mud/filter backwash solids) followed by filtration of the hypochlorite-treated material on a rotary vacuum filter. The filter cake is washed successively with HCl and fresh water. By means of this treatment sequence, the filter cake solids entrained mercury content is lowered to the point where EP-tox leachable mercury is below 12 ppb, enabling these portions of the K071 solid waste to be delisted.

This treatment procedure is in routine use at the Vulcan Chemicals, Port Edwards, Wisconsin, mercury cell chloralkali plant and is currently being installed at the B.F. Goodrich, Paducah, Kentucky, mercury cell chloralkali facility. The former plant's K071 waste has been fully delisted by EPA (including both the saturator insolubles, which are treated using a brine washing technique, and the brine purification-related muds treated as discussed under this option). The latter plant will be granted a conditional delisting pending acquisition of a suitable body of data applicable to a permanent delisting of its entire K071 waste stream by EPA. Data obtained during a recent EPA BDAT sampling and analysis effort at the Vulcan Chemicals, Port Edwards, Wisconsin, plant indicated that the pH adjustment, hypochlorite treatment, and filtration/washing steps result in a K071 waste that averaged less than 1 ppb mercury in the leachate when subjected to the EPA toxicity characteristic leaching procedure (TCLP) test (EPA 1987c).

A simplified schematic of the proposed option (3) applicable to both the NaCl and KCl K071 waste streams is shown in Figure 10.

The capital equipment requirements for both NaCl and KCl brine wastes treatment processes would be identical, including for each stream:

- Clarifier/Thickener (30 ft diameter x 10 ft high);
- pH adjustment tank (10,000 gallons), propeller agitator;
- Hypochlorite treatment tank (20,000 gallons), propeller agitator; and
- Rotary vacuum filter (100 sq ft. filtration area).

Together with associated instrumentation, piping, and pumps, the total installed cost for the Vulcan Treatment Process portion of option (3) for both the NaCl and KCl wastes is estimated to be $1.4 million. Annual direct operating costs for the two treatment lines (including labor, chemicals (H_2SO_4, HCl, calcium hypochlorite), power, water, and maintenance) is estimated as $300,000 per year. Annual savings by disposal of an estimated combined delisted brine purification waste of 1,000 tons per year at $33 per ton in a nearby lined sanitary landfill, as compared to present disposal of 2,500 tons per year of K071 combined

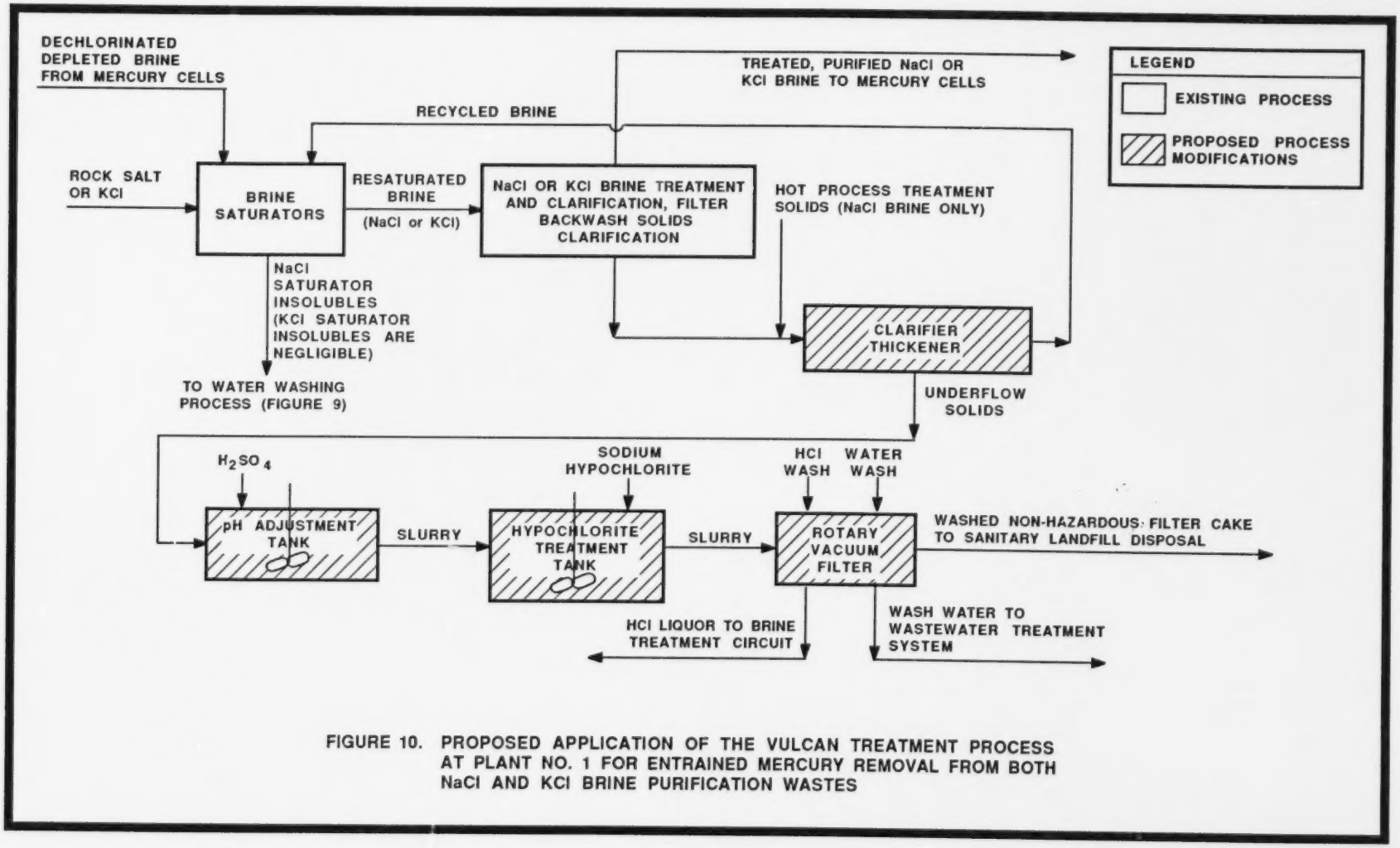

FIGURE 10. PROPOSED APPLICATION OF THE VULCAN TREATMENT PROCESS AT PLANT NO. 1 FOR ENTRAINED MERCURY REMOVAL FROM BOTH NaCl AND KCl BRINE PURIFICATION WASTES

brine purification waste in the Emelle, Alabama, hazardous waste landfill at $150 per ton, is $342,000 per year. Overall net operating savings for this portion of option (3) is therefore $42,000 per year. Combined with the respective investment cost and overall net savings of the saturator insolubles treatment portion of this option, the overall payback period is (1,400,000 + 500,000/42,000 + 262,000) or 6.3 years. This option therefore does not look as attractive from an economic standpoint as the previous treatment options; however, it is important to note that all of the treatment steps appear to have been proven and reduced to practice in other mercury cell chloralkali facilities. Plant No. 1 may, therefore, wish to give this approach further study.[1]

Summary of Postulated Options for Minimization of Listed Waste K071

A total of seven source reduction options were developed by the audit team at Plant No. 1 for listed waste K071, as well as three detoxification treatment options for this waste. Table 10 summarizes these options and results of the preliminary evaluation by both the audit team and plant personnel. One source reduction option (option E) and two treatment options (options (1) and (2)) appear worthy of detailed evaluation by Plant No. 1 for minimization of listed waste K071 at this site.

WMA AT PLANT NO. 2

Facility Description

Plant No. 2, located in the Southeast, is a mercury cell chloralkali plant built in 1966 and has a name plate capacity of 116,000 metric tons per year of chlorine. Sodium hydroxide (NaOH) is produced as a co-product and plant capacity is approximately 354 metric tons per day. Louisiana rock salt, received by barge, is the raw material used.

The chloralkali facility employs DeNora type mercury cells equipped with metal anodes. All of the chlorine produced is used captively in an adjacent chemical complex. The co-product NaOH is sold primarily to external customers in the Southeast.

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1 In this regard, Plant No. 1 personnel have expressed concern with the very high TDS in the Port Edwards plant wastewater effluent. The Port Edwards plant discharges approximately 20,000 mg/l of various soluble cations including sodium, potassium, calcium, and magnesium, as well as about 100,000 mg/l of chloride (the Vulcan process characteristically generates high levels of TDS). Plant No. 1 believes that its State permitting requirements would not allow such high levels of dissolved salts in its effluent.

Table 10. Summary of Postulated Options for Minimization of Listed Waste K071 at Plant No. 1

Option	Description	Type of option	Advantages	Disadvantages	Potential savings over present cost of waste disposal ($/yr)
A	Reduction of depleted brine dissolved sulfate level to minimize saturator insolubles generation	Source reduction	Reduce generation rate of saturator insolubles portion of K071 waste by as much as one-third. Save significant labor cost currently involved in periodic cleanout of saturators.	Depleted brine side stream treatment needed to reduce dissolved sulfate results in excessive precipitant cost as well as large additional generation of mercury-contaminated wastes.	-
B	Use of prepurified salt feed stock	Source reduction	Essentially complete elimination of mercury-contaminated K071 waste generation in NaOH production.	Unacceptable economics.	-
C	Use of solar salt as a feed stock	Source reduction	Significant reduction of mercury-contaminated K071 generation in NaOH production.	Unacceptable economics.	-
D(1)(c)	Removal of mercury from depleted brine prior to brine resaturation, using sulfide precipitation with disposal of mercury sulfide waste	Source reduction	Essentially complete elimination of mercury-contaminated K071 waste generation in NaOH production.	Commercially unproved process; creation of another K071 waste; unacceptable economics.	-

Table 10. (Continued)

Option	Description	Type of option	Advantages	Disadvantages	Potential savings over present cost of waste disposal ($/yr)
D(1)(b)	Removal of mercury from depleted brine prior to brine resaturation using sulfide precipitation, followed by mercury retorting and recovery from mercuric sulfide waste	Source reduction	Same as in D(1)(a).	Commercially unproven process; unacceptable economics.	-
D(2)	Removal of mercury from depleted brine prior to brine resaturation using ion exchange resin	Source reduction	Same as D(1)(a).	No commercially available resin available for handling harsh depleted brine environment without extensive pretreatment for chlorine removal; limited resin capacity and allowable brine flow rate require very large resin beds (unacceptable economics).	-
E	Conversion of mercury electrolytic cells to membrane electrolytic cells	Source reduction	Complete elimination of all mercury-bearing streams results in elimination of K071 and K106 wastes; preliminary economics indicate acceptable payback period (~2 years). Membrane technology commercially proven.	Detailed feasibility study using definitive base costs may show much worse payback than preliminary estimate. Space requirements for auxiliary equipment may be unavailable.	600,000

Table 10. (Continued)

Option	Description	Type of option	Advantages	Disadvantages	Potential savings over present cost of waste disposal ($/yr)
(1)	Use of a washing process to reduce the level of mercury in the K071 saturated insolubles below 12 ppb, enabling this waste to be delisted	Treatment	Simple, commercially-proven process that would allow delisting of a large portion of K071 waste. Favorable payback period (~2 years). Space availability at plant is not a problem.	Potential delay in achieving EPA delisting because of lengthy procedure involved.	360,000
(2)	Same as (1) for saturator insolubles coupled with NaSH treatment process for brine purification muds, enabling delisting of the entire K071 waste stream	Treatment	Same as in (1) for saturator insolubles; addition of process for brine muds still shows favorable payback period (2.3 years). Space availability at the plant for a combined treatment process is not a problem.	Sulfide treatment step for brine purification muds is commercially unproven. Lack of proven treatment process could delay up EPA delisting of the entire stream until adequate body of process data is available.	325,000
(3)	Same as (1) for saturator insolubles coupled with Vulcan Treatment Process for brine purification muds, enabling delisting of the entire K071 waste stream	Treatment	Same as (1) for saturator insolubles. Vulcan process is commercially proven and is expected to be BDAT for K071 waste. Space availability at plant for combined treatment process is no problem.	Economics of Vulcan process for combined NaCl and KCl brine stream purification muds appears unfavorable at this time. Vulcan process may also generate higher TDS in effluent from Plant No. 1 than State will allow.	-

Plant No. 2 presently generates approximately 5,400 tons per year of listed waste K071, including about 1,080 tons per year of saturator insolubles and 4,320 tons per year of brine treatment sludges. The plant also generates about 75 tons per year of listed waste K106 (mercury-bearing wastewater treatment sludges). All of this waste is currently sent offsite to hazardous waste landfills. The focus of this study is to propose ways to reduce or eliminate the generation of K071 and K106 wastes.

Process Description

Plant No. 2 produces both NaOH and a chlorine co-product in a mercury cell electrolytic production line. During electrolysis of sodium chloride brine in the mercury cells, chlorine gas is formed at the anodes and is collected, cooled, and dried by passing through sulfuric acid and then compressed, liquefied, and stored for shipment. Simultaneously, in the cells, a sodium-mercury amalgam is formed at the flowing mercury cathodes. Mercury leaving the cells, which contains the amalgam, is subsequently reacted with water in units called denuders. The reaction converts the amalgam to mercury metal, a 50 percent NaOH solution and hydrogen gas. The hydrogen gas is collected, partially shipped to other production units in the chemical complex, and partially burned for fuel; the NaOH solution is further processed before being shipped to customers, and the mercury is returned to the cells. Figure 11 is a simplified schematic of the NaOH/chlorine production process.

The spent brine leaving the mercury cells contains about 22 percent sodium chloride versus 25 percent in the incoming brine. This depleted brine typically containing 20 ppm dissolved mercury (primarily as mercuric chloride) is further acidified with hydrochloric acid (to pH 2.5) and is then dechlorinated using vacuum flash tanks. The chlorine released is collected and combined with that generated in the mercury cells for further processing. The dechlorinated brine is then pumped to the initial portion of the process, where rock salt is added to form a resaturated brine. Rock salt is dissolved in the dechlorinated brine from the mercury cells. Table 11 presents a typical rock salt analysis at Plant No. 2. The depleted brine has 20 percent NaOH solution blended with it prior to entering the dissolver. The NaOH addition adjusts pH from ~2.5 to near neutral (pH 5 to 6) in order to avoid dissolution of silica (as silicates) in the brine. Rock salt (NaCl) dissolution occurs in a saturator (or dissolver) tank, where the flow of salt is countercurrent to the brine flow. No agitation is used in the dissolver tank. In this operation, the sodium chloride dissolves in the brine and the insolubles present in the rock salt fall to the bottom of the saturator vessel. These insolubles include clay and mineral components of the salt feed, together with precipitated materials formed in the

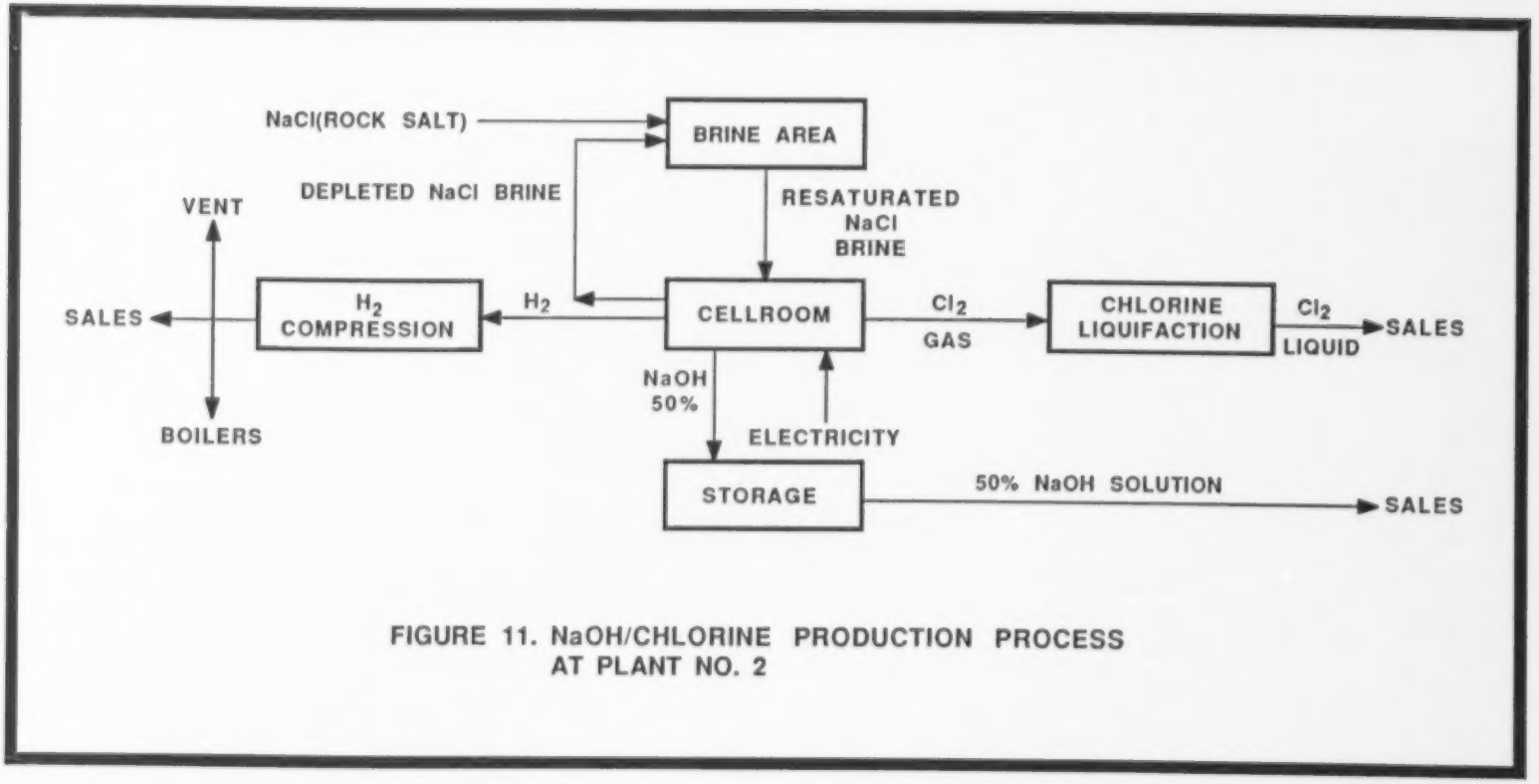

FIGURE 11. NaOH/CHLORINE PRODUCTION PROCESS AT PLANT NO. 2

Table 11. Typical Analysis of Rock Salt Used at Plant No. 2

Component	Concentration**
Bromine	56
Carbon organic	15
Chlorate as $NaClO_3$	<1.0
Chloride as NaCl	97.7 percent
Fluorine	<1.0
Iodine	<0.5
Silicon	<10
Sulfate as Na_2SO_4	1.44 percent
Aluminum	0.65
Barium	<1.0
Calcium	3900
Chromium	0.028
Cobalt	<0.01
Copper	0.037
Iron	3.2
Lead	0.38
Magnesium	18
Manganese	1.5
Mercury	0.017
Molybdenum	<0.05
Nickel	0.054
Potassium	53
Strontium	10
Titanium	2.5
Vanadium	<0.5
Zinc	3.9
H_2O insolubles	0.22 percent
Loss @ 110°C	0.065 percent
Phosphate	1.2

*Analysis as of May 1981; Plant No. 2 in-house data.
**Units of concentration are ppm unless otherwise noted.

dissolution step and small amounts of entrained mercury. The dissolution of the salt occurs in brine at a temperature of about 70°C.

Plant No. 2 has two dissolver tanks in parallel, one of which is in use at any given time and the other on standby. The dissolver tanks used are 45 feet in height and 28 feet in diameter, and are cone-shaped at the base. The accumulated saturator insolubles are periodically sluiced from the bottom of these tanks for treatment and disposal.

The resaturated brine flows by gravity to a series of four treatment tanks where sodium carbonate solution is added. Calcium, magnesium, and iron ions are present in the brine precipitate as calcium carbonate and magnesium and iron hydroxides, respectively. These precipitates are removed in the treated brine clarifiers. The clarifier overflow is then passed through pressure leaf filters to remove residual solids, and the filtered brine is then pumped to the mercury cells. The brine clarifier underflow, containing the precipitated solids and small amounts of entrained mercury (a second form of K071 waste), is fed to the K071 waste treatment system.

The clarification and filtration operations are carried out at 60 to 70°C. The clarifier used is 80 feet in diameter and 15 feet in height. The pressure leaf filters are periodically backwashed with brine to flush out accumulated impurities. The filter backwash stream (another portion of the K071 waste since it also contains entrained mercury) is sent to the K071 waste treatment system as well.

Waste Stream Description

There are two sources of listed waste K071 in Plant No. 2: (1) mercury-contaminated saturator insolubles and (2) brine treatment muds from the brine purification portion of the process. At Plant No. 2 these waste streams consist of the following:

(1) Brine saturator insolubles consist of gypsum, sodium sulfate, silica, and calcium carbonate, as well as less than 1 percent undissolved salt. Trace quantities of mercury (both soluble and insoluble) of up to 5 ppm (dry basis) are also found in this waste. About 1,080 tons per year (as a 40 percent moisture-60 percent solids material) of these insolubles are generated at Plant No. 2.

(2) Brine purification muds are made up mostly of calcium carbonate, with smaller quantities of gypsum and less than 1 percent salt and sodium sulfate. Mercury levels present are below 30 ppm

(dry basis). About 4,320 tons per year (as a 40 percent moisture-60 percent solids material) of these muds are generated at Plant No. 2, including approximately 4,120 tons per year of brine clarifier underflow solids and 200 tons per year of filter backwash solids.

The saturator insolubles and brine purification muds are combined at present prior to disposal; however, the plant is undergoing significant modifications to the K071 waste treatment system, as is described in detail in the Waste Management Profile section below.

Table 12 presents typical analyses of the K071 brine-related wastes.

Current Waste Management Profile (in Effect Until the Fall of 1987)

Following the selection of Plant No. 2 for a WM audit, the audit team made a pre-audit plant visit on February 24, 1987, and learned at that time (and in more detail during a subsequent visit by plant personnel to the audit team offices), that waste management practices for the K071 wastes were undergoing significant change. The plant had recently decided to install its version of the Vulcan Treatment Process for treatment of all the brine-related K071 wastes.[1] This process (when fully operational) will replace the current practice of dewatering all of the K071 wastes (including the saturator insolubles and brine purification wastes) on a rotary vacuum filter and shipping the K071 waste offsite to a hazardous waste landfill for disposal. The revamped waste management scheme for Plant No. 2 K071 waste is described below.

Revamped Waste Management Operation Based on Current Delisting Effort

Officials as Plant No. 2 have recently applied to EPA for a conditional delisting of their treated K071 wastes based on installing and operating their version of the Vulcan Treatment Process. A conditional exclusion (notice of which will appear in the Federal Register) is expected to be obtained from EPA by the fall of 1987. At that time, plant management will begin to assemble the needed treatment data to gain a final delisting of the treated wastes. Corporate plans call for disposal of the treated brine purification wastes in a nearby sanitary landfill following receipt of the EPA conditional exclusion.

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1 A K071 waste treatment process developed by the Vulcan Chemicals, Port Edwards, Wisconsin, chloralkali facility and available to the mercury cell chloralkali industry. Operational information and mercury levels data in this report were obtained from the Vulcan delisting petition and its amendments.

Table 12. Total K071 Raw Waste Analyses at Plant No. 2 (Dry Basis)*

Sample Location and Date: Saturator insolubles - 7/23/80

Analysis	Units	Analysis
Mercury	ppm	3.4
Sodium chloride	percent	<1
Calcium sulfate	percent	62
Calcium carbonate	percent	16
Sodium sulfate	percent	<1
Insolubles (silica)	percent	20

Sample Location and Date: Brine clarifier solids - 7/23/80

Analysis	Units	Analysis
Mercury	ppm	26.5
Sodium chloride	percent	<0.1
Calcium sulfate	percent	17.9
Calcium carbonate	percent	82.1
Sodium sulfate	percent	<0.1

Sample Location and Date: Backwashed solids from brine filters - 7/29/80

Analysis	Units	Analysis
Mercury	ppm	14.8
Sodium chloride	percent	<0.1
Calcium sulfate	percent	18.2
Calcium carbonate	percent	81.8
Sodium sulfate	percent	<0.1

*Source: Plant No. 2 in-house data.

For the K071 treatment process as installed at Plant No. 2 and expected to be fully operational by the fall of 1987, the following treatment steps will be included:

- The saturator insolubles will be collected every few days in a dumpster, with each batch then washed using depleted acidic brine. The mercury compounds present in the saturator insolubles dissolve in the brine. The brine will then be drained from the washed saturator insolubles and recycled to the mercury cell process. Residual levels of mercury in the treated insolubles should be about 3 ppm based on results obtained with the process at the Vulcan Chemicals Plant in Port Edwards, Wisconsin. The treated saturator insolubles are expected to show less than 12 ppb in the EP-tox leachate from this material.

- The brine purification muds (both brine clarifier underflow solids and brine filter backwash solids) will be collected and pumped to a pH adjustment tank for treatment. The pH adjustment tank serves as a storage vessel to equalize feed rate fluctuations, and as a reaction vessel where spent sulfuric acid (a chlorine drying by-product) is added. The brine treatment precipitated solids are acidified to a pH of 2 to 3 to promote the growth and precipitation of calcium sulfate crystals. All calcium carbonate is chemically converted to calcium sulfate and magnesium hydroxide is converted to magnesium sulfate in the acidification step. The calcium and magnesium sulfates' crystal structure characteristics allow these materials to be more readily filtered, thereby enhancing solubilized mercury removal.

- The acidified calcium sulfate slurry from the pH adjustment tank will be further treated with sodium hypochlorite (a chlorine liquefaction/emergency scrubber by-product) to solubilize the mercury in a hypochlorite treatment reactor. In this tank, the addition of sodium hypochlorite will ensure conversion of the mercury to a soluble mercuric form. Any residual chlorine generated in this tank will be vented back to the plant chlorine recovery system. Following the hypo addition step, the treated slurry will be pumped to a rotary vacuum filter that separates the solubilized mercury from the treated solids, the former then being discharged in the filtrate, which is sent to the wastewater treatment system.

- A spray wash system on the rotary vacuum filter will further reduce mercury content by ensuring solubilization of mercury and by removing mercury-bearing liquids from the filter cake. The spray wash system will consist of a low-pH acid wash (a pH of 4

achieved by the use of a dilute HCl solution), followed by two water washes. The filter cake solids will have thus been successively treated with sulfuric acid and sodium hypochlorite, and then washed under conditions comparable to an extraction process likely to be found in any landfill under worst-case conditions. Residual mercury level in the filter cake is expected to be about 2.5 ppm based on data supplied by the Vulcan Chemical, Port Edwards, Wisconsin, plant. EP-tox leachate from the filter cake solids is expected to be <12 ppb.

Figure 12 presents a simplified schematic of the K071 treatment process currently becoming operational at Plant No. 2.

Rationale for No Development of Waste Minimization Options

As discussed above, management at Plant No. 2 had made a decision on handling its various brine purification wastes so as to remove them from the K071 waste category. The plant is installing the Vulcan brine sludge treatment process and expects that it will be fully operational by the fall of 1987.

In selecting this technology, the facility management had also investigated a number of other options, such as a simple washing process, purchase of prepurified salt, and potential in-situ brine treatment processes for removal of mercury from the brine. All of these alternative options were rejected in favor of the Vulcan process because of either cost or technological factors.[1]

Since the treatment technology to detoxify K071 wastes has already been selected and installed at Plant No. 2, no additional WM options were considered for this waste.

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1 In addition to findings similar to most of those presented above for Plant No. 1 on source reduction options for K071 waste, i.e., technically and/or economically infeasible options that caused their rejection by Plant No. 2, economic studies by the latter on adoption of the Vulcan K071 waste treatment process showed that a savings of approximately $16,000 per week would be available if the K071 waste was delisted by EPA, allowing disposal of this material in a local sanitary landfill (Personal Communication from Plant No. 2 personnel).

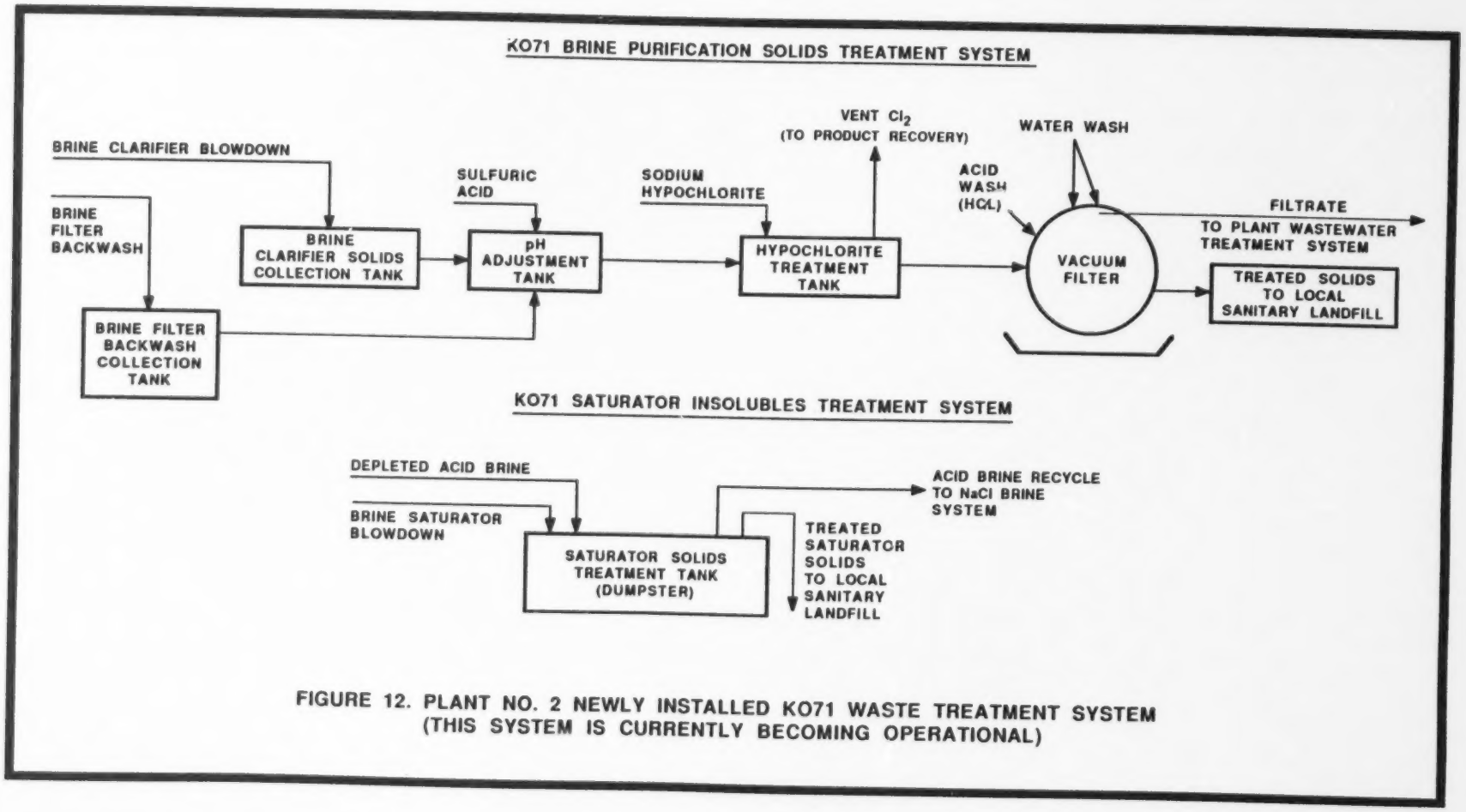
K071 BRINE PURIFICATION SOLIDS TREATMENT SYSTEM
BRINE CLARIFIER BLOWDOWN
BRINE FILTER BACKWASH
BRINE FILTER BACKWASH COLLECTION TANK
BRINE CLARIFIER SOLIDS COLLECTION TANK
SULFURIC ACID
pH ADJUSTMENT TANK
SODIUM HYPOCHLORITE
HYPOCHLORITE TREATMENT TANK
VENT Cl_2 (TO PRODUCT RECOVERY)
WATER WASH
ACID WASH (HCL)
VACUUM FILTER
FILTRATE TO PLANT WASTEWATER TREATMENT SYSTEM
TREATED SOLIDS TO LOCAL SANITARY LANDFILL
K071 SATURATOR INSOLUBLES TREATMENT SYSTEM
DEPLETED ACID BRINE
BRINE SATURATOR BLOWDOWN
SATURATOR SOLIDS TREATMENT TANK (DUMPSTER)
ACID BRINE RECYCLE TO NaCl BRINE SYSTEM
TREATED SATURATOR SOLIDS TO LOCAL SANITARY LANDFILL

FIGURE 12. PLANT NO. 2 NEWLY INSTALLED K071 WASTE TREATMENT SYSTEM
(THIS SYSTEM IS CURRENTLY BECOMING OPERATIONAL)

Summary and Discussion

The K071 waste generated at mercury cell chloralkali plants is a large-volume waste averaging several thousand tons per year of inert material (principally calcium carbonate and calcium sulfate) for the typical plant, and contaminated with levels of mercury in the 30 ppm range. At Plant No. 1, less than 5 pounds of mercury per day are entrained in approximately 30,000 pounds per day of inerts. The depleted brine stream that carries the entrained mercury to the resaturation and subsequent brine purification step is also a large stream, typically amounting to 1,000 to 2,000 gallons per minute circulation rate and containing 5 to 10 ppm entrained mercury. In-plant removal or recovery of mercury from these streams is clearly not economically feasible, although this may be possible to accomplish from a technical standpoint. Replacement of the rock salt feed material with pre-purified salt (in order to avoid the generation of K071) also is not economically feasible.

In summary, the results of WMAs conducted at Plants No. 1 and 2 by the EPA-sponsored audit team clearly indicated that WM options (source reduction and/or recycle options) for minimization of K071 waste at mercury cell chloralkali plants are extremely limited. The only technically and economically feasible source reduction option available to Plant No. 1 to eliminate generation of K071 waste is highly capital intensive, i.e., an investment of approximately $20 million to replace the mercury electrolyic cells with membrane cells (and required auxiliary equipment). Installation of this option by Plant No. 1 would result in a potential savings of about $600,000 annually in disposal cost of K071 and K106 wastes in hazardous waste landfills, and a payback period of less than 3 years. No WM options were developed at Plant No. 2 since this facility is currently phasing in a K071 waste treatment process (the Vulcan Treatment Process), which will result in this waste's being delisted by EPA and allow disposal in a local sanitary landfill.

Since the audit team's investigations in the desired areas of WM for the K071 waste were relatively nonproductive, consideration was also given to treatment options. A commercially-established washing process for the saturator insolubles portion of the K071 waste (treatment option (1)), either used alone or coupled with an experimental sulfide treatment process for the brine purification solids portion of this waste (treatment option (2)), was considered both technically and economically feasible in the preliminary evaluation. More pilot-scale effort will be necessary to establish operational parameters for the sulfide treatment process. Potential annual savings in hazardous waste disposal costs for Plant No. 1 would range from $325,000 per year (treatment Option (1)) to $380,000 per year (Treatment Option (2)), with payback periods of less than 2.5 years in either case.

By removing mercury to low ppm levels in the treated K071 waste (<5 ppm), TCLP (or EP-tox) leachate has been shown to be $\leq$12 ppb, a level sufficiently low to allow delisting of this waste by EPA, thus enabling a mercury cell chloralkali plant to dispose of the treated waste in a sanitary landfill. Approximately 14 such plants may be able to benefit from this approach at the present time.

SECTION 5

LISTED WASTE K106 - WMA CASE STUDIES

The focus of this set of case studies is to propose ways to reduce or eliminate the generation of listed waste K106. This waste is defined in 40 CFR 261.32 as follows:

- K106: Wastewater treatment sludge from the mercury cell process in chlorine production.

Two facilities were selected as host sites for WMAs at generators of listed waste K106. The two plants involved are mercury cell chloralkali facilities located in the Southeast. Background information on the generation of listed waste K106 at mercury cell chloralkali plants can be found in two EPA documents on this waste (EPA 1980, EPA 1980a). In this report, the two plants studied are designated as Plant No. 1 and Plant No. 2.

WMA AT PLANT NO. 1

Facility Description

(See Section 4)

Process Description

(See Section 4)

Waste Stream Description

A common wastewater treatment system is used to handle all mercury-containing wastewaters from both the NaOH and KOH production lines. The streams with the highest concentrations of mercury and volumes of water are cellroom washwater and mercury cell end box purge water. Waste streams that contain little or no mercury contamination, such as rainwater collected in the brine purification area, are also treated. The wastewater treatment consists of the addition of hydrazine to 60 to

90 gpm of alkaline wastewater. The normal concentration of hydrazine in the wastewater during treatment is 0.5 ppm. With exposure to air, hydrazine spontaneously decomposes to form water and nitrogen gas. The hydrazine reacts with dissolved mercury salts present in the wastewater to yield mercurous hydroxide, which precipitates. Filtration of the treated wastewater generates a sludge that is primarily composed of carbon (used as filter precoat material), diatomaceous earth (filter aid), water (approximately 50 percent of the cake weight), dirt from the various sumps, and the collected mercury (as mercurous hydroxide). The concentration of hydrazine in the treated sludge has been found to be below detectable limits. This sludge is the listed hazardous waste K106, with mercury levels typically in the 0.5 percent range. The treated wastewater effluent from the system contains approximately 0.04 to 0.08 ppm mercury, and is discharged to a river under an NPDES permit with a mercury limit of 0.082 pounds per day (0.041 kg/day) (monthly average). An average of about 20 tons per year of K106 waste is generated at the facility. Figure 13 is a simplified schematic of the existing wastewater treatment system at Plant No. 1.

Current Waste Management Profile

The K106 waste is recovered as a filter cake from a plate and frame filter press in the wastewater treatment area of Plant No. 1. This waste is containerized and sent to a hazardous waste landfill for final disposal.

Postulated Waste Minimization Options and Preliminary Analysis of Their Technical and Economic Feasibility

Discussions were held with Plant No. 1 personnel on the potential for minimizing or eliminating the generation of K106 waste from plant wastewater treatment. Results of these discussions and further evaluations by the audit team are presented below.

Source Reduction Options

As described above, K106 waste at Plant No. 1 derives from the various wastewaters collected from plant operations, as well as rainwater runoff from production areas involved with mercury or mercury compounds processing. There appears to be no feasible way for the plant to minimize or modify the process-related sources of this wastewater, as these sources have unavoidable impurities buildup requiring a periodic purge, e.g., wastewater from mercury cell end boxes. The other sources of wastewater are housekeeping-related, e.g., cell room wash downs; accidentally generated, e.g., brine spills; or incidentally generated, e.g., rainwater runoff. Therefore, it appears that source reduction options are not available to reduce or eliminate this waste.

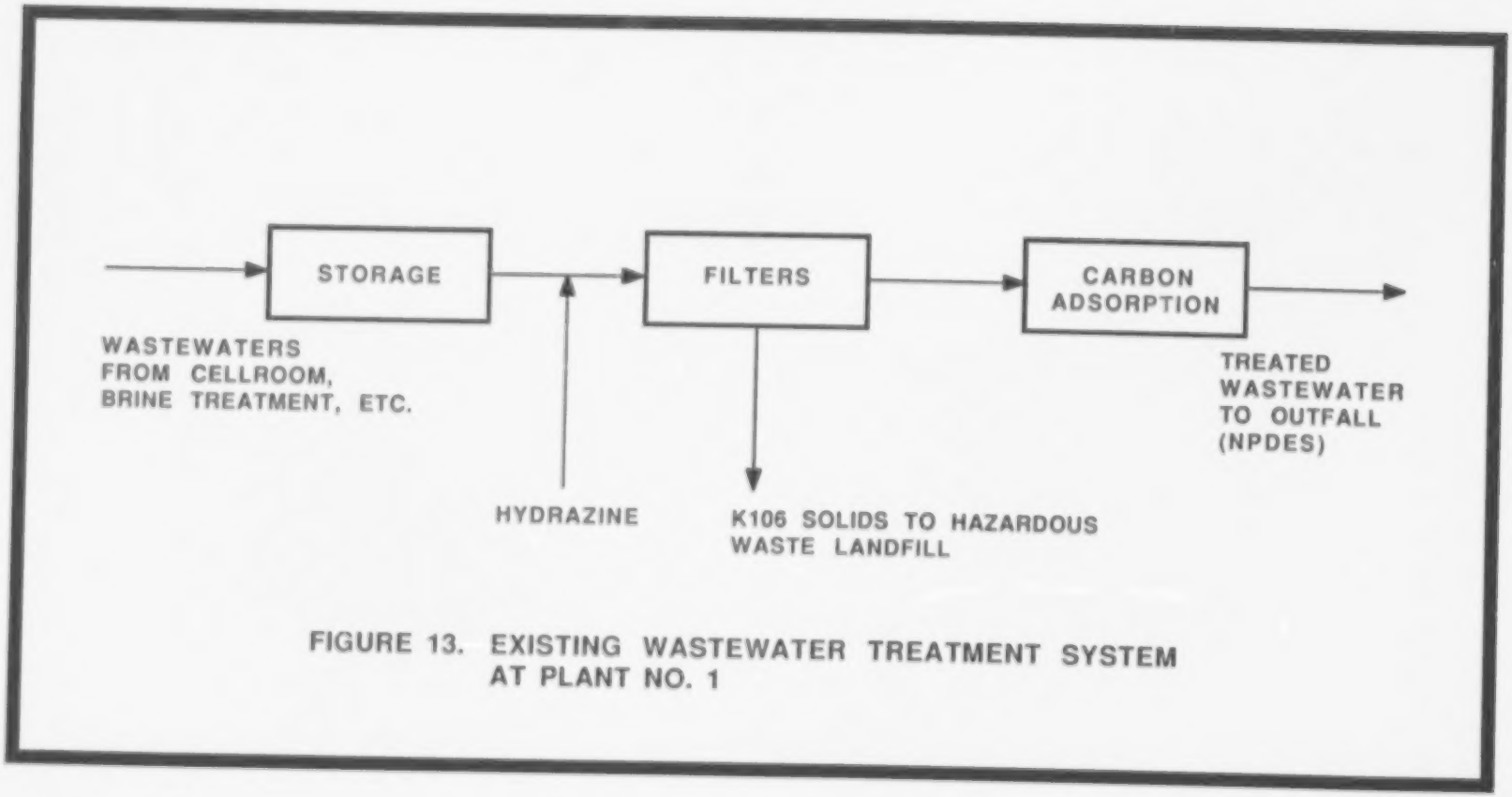

FIGURE 13. EXISTING WASTEWATER TREATMENT SYSTEM AT PLANT NO. 1

Recycle/Reuse Options

The raw mercury-bearing wastewaters generated in Plant No. 1 appeared to be amenable to one recycle/reuse option for mercury recovery and recycle to the plant. The wastewater treatment sludge (K106) generated in the wastewater treatment process seemed to be amenable to one recycle/reuse option for mercury recovery and recycle to the plant. These two options are discussed below:

(a) Use of a suitable ion exchange resin for removal of mercury from the combined wastewater generated by Plant No. 1, followed by recovery of the mercury in a form suitable for recycle to the mercury cell system. In this proposed option, a suitable ion exchange resin (such as the IMAC TMR resin manufactured by Akzo Zout Chemie, Rotterdam, The Netherlands) would be used to remove mercury from the combined wastewater stream, following suitable pretreatment of the wastewater to enable the resin to function efficiently. This resin is claimed to be in use in over 20 mercury cell chloralkali plants worldwide for mercury removal from wastewater (DeJong and Rekers 1974).

In chloralkali plant wastewater, mercury can occur as metallic and ionic mercury, e.g., mercuric chloride. There can be large variations in pH, salt, and chlorine content, and significant amounts of solids present, which could plug the ion exchange resin. In order to accommodate these variables, the proposed ion exchange mercury recovery process would incorporate the following pretreatment steps in treating an average of 75 gpm of wastewater with an average mercury level of 10 ppm:

- Oxidation/pH adjustment using HCl and hypochlorite;
- Filtration using sand filters;
- Two-stage dechlorination using $NaHSO_3$ (or Na_2SO_3) followed by activated carbon treatment; and
- Ion exchange treatment consisting of two beds of IMAC TMR resin in series. This process includes mercury recovery, desorption of bound mercury as mercuric chloride, and resin regeneration. The long cycle time of the resin is claimed to provide ample cycle time to regenerate the first column before the second column breaks through.

The existing wastewater cleanup process (described above) would act as a backup system in the event that the ion exchange process had to be taken offline because of sudden resin failure. Resin failure can occur

as a result of sudden excursions in the free chlorine level of the wastewater, which are unable to be controlled by the pretreatment system. The resulting excess chlorine could destroy the activity of the resin.

With regard to ion exchange economics, a recent Akzo quote (1985 dollars) for a complete plant to handle a 250 gpm wastewater treatment rate[1] has been prorated for the average 75 gpm feed rate in Plant No. 1, using the 0.6 factor. The plant design referred to treated a feed stream with an average 10 ppm mercury content and produced an effluent containing <5 ppb mercury. The adjusted plant cost for the 75 gpm feed site at Plant No. 1 is $1.7 million installed. Annual direct operating costs were estimated as $350,000 per year, including labor, chemicals, resin replacement, power, and maintenance costs. Present disposal costs of the mercury-bearing waste from wastewater treatment, based on a maximum of 40 tons per year of K106 waste (containing approximately 0.5 percent mercury) at $150 per ton sent to the present hazardous waste disposal site, are estimated as $6,000 per year. Maximum recovered value of mercury at $6 per lb (as elemental mercury) is estimated as $2,000 per year. Overall savings using the proposed recycle option for the mercury in the K106 waste would be about $8,000 per year. Since the direct operating costs of $350,000 per year far exceed the savings available, this recycling/reuse option is not considered economically viable.

(b) The use of a retorting process to treat the K106 waste for recovery of elemental mercury and disposal of the mercury-free residue as a delisted non-hazardous waste in a nearby approved sanitary landfill.

Between 20 and 40 tons per year of wastewater treatment sludge (K106) are generated at Plant No. 1 as a filter cake. This material contains 50 percent water, 49 plus percent inerts including: filter aid (diatomaceous earth), carbon from filter precoating, and dust from the various wastewater collection sumps, as well as approximately 0.5 percent mercury (primarily as mercurous hydroxide from the hydrazine treatment step). A recycle option is proposed wherein this material would be retorted in a special retort in use in other mercury cell chloralkali plants of Plant No. 1's parent corporation. The retort operates under vacuum in an inert steam-injected atmosphere and is gas-fired. The mercurous hydroxide decomposes at a temperature of 700 to 800°F,

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1 Personal Communication, Mr. H.G.J. Durville, Akzo Engineering, Rotterdam, Netherlands, to plant personnel at Plant No. 2, February 12, 1985.

forming mercury vapor and water. Mercury condensation is accomplished by cooling, using a water-injected venturi scrubber. The residual noncondensable vent gases are passed through an activated carbon column for final trace mercury removal. Based on a limited number of plant-scale tests of this process, leachate from the residue from the retorting step has been shown to contain less than 12 ppb mercury by EP-tox test, so that the retort residue should be able to be delisted by EPA. A small schematic of the proposed process is shown in Figure 14.

A retort to recover approximately 0.2 ton per year of mercury (400 lb/year) from a maximum of 40 tons per year of K106 waste would have to operate intermittently because of the small quantity of waste material involved. It is proposed to accumulate the filter cake over a 90-day period, at which time the retort would process this waste on a batch during the day shift (8 hours per day) at the rate of about 1,000 pounds per day. The retort system is estimated to cost $100,000 installed. Annual direct operating cost (including fuel, power, labor, and maintenance) for 180 days per year operation, is estimated as $36,000 per year. With maximum recovered mercury valued at $2,400 per year ($6 per lb) and savings in hazardous waste landfill disposal costs at $6,000 per year (see discussion under recycle option (a)), there is a net deficit in operating this unit (6,000 + 2,400 - 36,000) of $27,600 per year, so that no payback period is available. This option is thus not economically viable unless the retort was required for processing a sufficient volume of contaminated mercury (spills) or other mercury-contaminated waste materials. By increasing the retort throughput in this manner, mercury recovery from K106 waste could be potentially economical.[1]

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1 In point of fact, Plant No. 1 has recently submitted a petition for proposed conditional delisting of K106 waste to EPA (July 20, 1987) using this retorting technique. Based on limited plant-scale data, the petition claims that EP-tox levels will be below the level specified for mercury in 40 CFR 261.24, Table 1 (0.2 ppm), that no other EP-tox metals exceed the Table 1 limits, and that there are no Appendix VIII hazardous constituents present above detectable limits. The state environmental authorities have advised Plant No. 1 that the proposed retorting plant will not require an air emission permit. The petition provides no specifics on retorting operation conditions nor on whether the K106 waste would be the sole material processed in the retort. This petition thus confirms the audit team's belief in the technical viability of the mercury retorting option, but leaves open the question of the economic viability of this process.

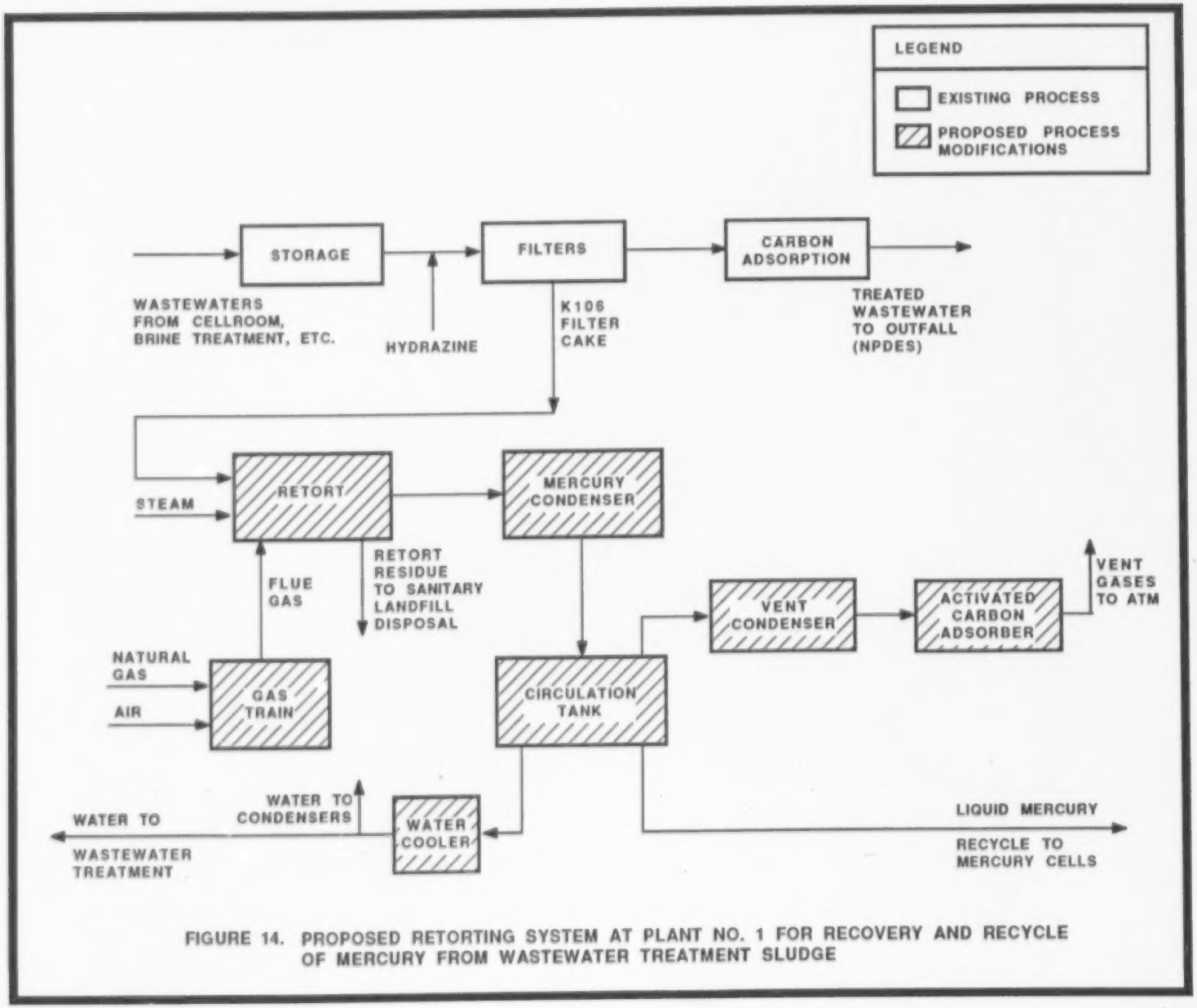

FIGURE 14. PROPOSED RETORTING SYSTEM AT PLANT NO. 1 FOR RECOVERY AND RECYCLE OF MERCURY FROM WASTEWATER TREATMENT SLUDGE

Treatment Options

While treatment is not a WM option, there do not appear to be any economically viable source reduction or recycle/reuse options available to minimize or eliminate the generation of K106 waste at Plant No. 1. A treatment option wherein the K106 waste could be detoxified enabling it to be delisted and thus be disposed of in a sanitary landfill, may be the only technically and economically viable alternative to the present disposal of K106 in a hazardous waste landfill. One such proposed treatment option is presented below.

(c) Use of a solidification/stabilization technique to render the K106 waste non-hazardous and permit disposal in a sanitary landfill following suitable delisting.

In this proposed option, the K106 filter cake produced as a result of wastewater treatment at Plant No. 1 would be combined with a cementatious material such as lime kiln or cement kiln dust in order to solidify the waste material in an insoluble matrix, which would pass the EP-tox test for leachable mercury, i.e., <12 ppb mercury for EPA delisting. Preliminary laboratory work in connection with the current EPA BDAT effort in mercury cell chloralkali plant hazardous waste treatment, indicates that it may be possible to immobilize the mercury in the K106 waste, using this method. Preliminary results from TCLP leach tests of a blend of one-third by weight lime kiln dust and two-thirds by weight K106 waste, showed leachable mercury to be less than 10 ppb.[1] The solidified material met the 50 psi strength criterion as a low-strength concrete. The results shown here, while preliminary in nature, appear to offer a good possibility for a treatment alternative to disposal of K106 waste in hazardous waste landfills.

Preliminary economics were developed for a solidification/stabilization system based on the results given above. Blending of lime kiln dust and K106 waste would be done on a concrete pad, using a small dedicated concrete mixer. The blending operation could be done once per week, blending approximately 0.5 ton of the waste with about 0.25 ton of lime kiln dust. The lime kiln dust would be stored in a pre-fabricated metal building holding about 3 months supply (3 to 5 tons) of this

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1 Personal Communication, Mr. M. Arozarena, PEI, Inc., Cincinnati, Ohio, April 29, 1987. The K106 waste was produced by wastewater sulfide treatment at the Vulcan Chemical Plant, Port Edwards, Wisconsin, chloralkali facility. This technique would have to be applied to other K106 wastes and be given more in-depth testing to establish its viability.

material in bags. The blended material would be allowed to cure on a concrete storage pad for 1 to 2 months prior to being shipped offsite to an approved sanitary landfill.[1]

Installed cost for a suitable prefabricated storage building to hold the lime kiln dust is estimated as $2,000. A small, portable concrete mixer is estimated to cost approximately $3,000. It is believed that there is adequate space on the existing concrete sludge holding pads which could be segregated in order to perform the blending and hold the solidified material prior to shipment offsite for disposal. Annual operating cost (including labor, lime kiln dust, fuel, and maintenance) is estimated as $3,000 per year. Disposal cost for the delisted K106 waste would be approximately $1,500 per year, based on disposal in a nearby approved sanitary landfill, as compared to a disposal cost of $6,000 per year for the present disposal cost in a hazardous waste landfill. Overall annual savings available if the proposed treatment option was implemented, is estimated as $1,500 per year, with a payback period of slightly over 3 years. This option thus appears to be worthy of further evaluation, including sufficient research and development to establish the appropriate operating parameters for the solidification/stabilization reaction involving K106 waste and lime kiln dust.

WMA AT PLANT NO. 2

Facility Description

(See Section 4)

Process Description

(See Section 4)

Waste Stream Description

A common wastewater treatment system is used to handle all mercury-containing wastewaters from the NaOH production line, as well as rainwater runoff, cell room wash down streams, leaks, and spills. The streams with the highest concentrations of mercury and volumes of water are cellroom wash water and mercury cell end box purge water. Waste

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1 This material, following submission of suitable TCLP leachate data for EPA, would be delisted and thus be suitable for disposal in a sanitary landfill. It is assumed that a permit would be required to operate as a TSD facility in order to carry on this operation.

streams that contain little or no mercury contamination, such as rainwater collected in the brine purification area, are also treated. The wastewater treatment consists of the addition of sodium hydrosulfide (NaSH) to 250 to 300 gpm of wastewater, which has been acidified to pH 2.5 - 3.5 using sulfuric acid. The NaSH reacts with the dissolved mercury salts present in the wastewater to yield mercuric sulfide, which precipitates. Two-step filtration of the treated wastewater (including filtering the precipitated sulfide/filter aid slurry through a precoated porostone filter followed by periodic filter back wash and final filtration of the backwash through a plate and frame filter press) generates a filter cake that has the following approximate composition:

Filter cake component	Approximate weight percent
Water	40
Filter Aid/Carbon	54
Brine Muds/Sump Dirt	3
Residual Sulfide	<0.5
Mercury	1-3

This filter cake is the listed hazardous waste K106. Figure 15 is a simplified schematic of the existing wastewater treatment system at Plant No. 2.

Current Waste Management Profile

The wastewater effluent from the system (following treatment through an activated carbon bed system) is discharged to a river under an NPDES permit with a total daily average mercury limit of 0.032 kg/day (0.07 lb/day) and a total daily maximum mercury limit of 0.073 kg/day (0.16 lb/day).[1] About three drums per week (75 tons per year of K106 filter cake) are generated at Plant No. 2. This material is currently disposed of, with the K071 waste being sent a hazardous waste landfill. However, when the K071 waste treatment system becomes fully operational in the fall of 1987, disposal costs for this small volume of hazardous waste could range up to $800 per ton because of the low volume and great distance to the disposal site. As a result, Plant No. 2 is interested in developing alternative WM options or detoxification treatment technologies for this waste (the latter allowing the waste to be delisted).

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1 Spent activated carbon is periodically removed from the system and sent to a hazardous waste landfill for disposal.

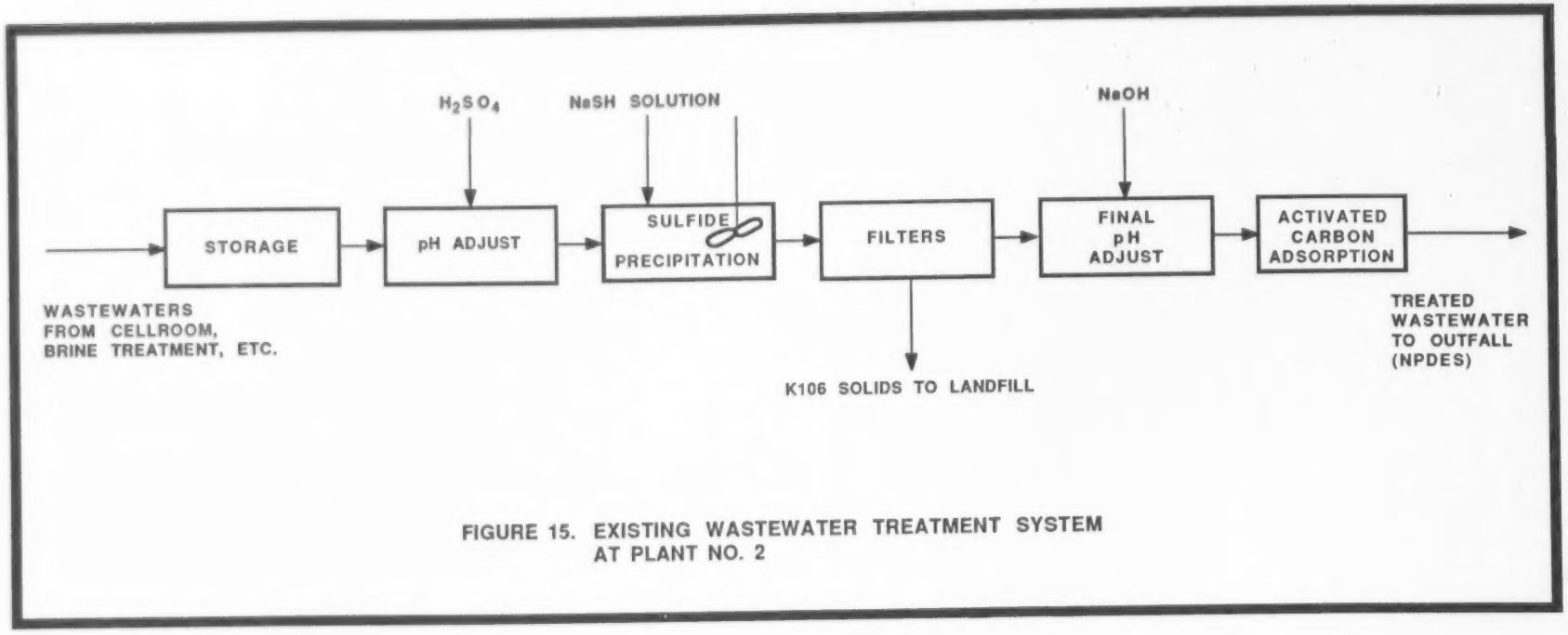

FIGURE 15. EXISTING WASTEWATER TREATMENT SYSTEM AT PLANT NO. 2

Postulated Waste Minimization Options and Preliminary Analysis of Their Technical and Economic Feasibility

Discussions were held with Plant No. 2 personnel on the potential for minimizing or eliminating the generation of K106 waste from plant wastewater treatment. Results of these discussions and further evaluations by the audit team are presented below.

Source Reduction Options

As described above in Section 5 under source reduction options for K106 waste generated at Plant No. 1, the identical wastewater generation situation at Plant No. 2 precludes development of any source reduction options to reduce or eliminate this waste.

Recycle/Reuse Options

The raw mercury-bearing wastewaters generated in Plant No. 2 appeared to be amenable to one recycle/reuse option for mercury recovery and recycle to the plant. The wastewater treatment sludge (K106) generated in the wastewater treatment process seemed to be amenable to one recycle/reuse option for mercury recovery and recycle to the plant. These two options are discussed below:

(d) Use of a suitable ion exchange resin for removal of mercury from the combined wastewater generated by Plant No. 2, followed by recovery of the mercury in a form suitable for recycle to the mercury cell system. This option would be carried out in an identical fashion to that described under option (a) in Section 5, above, for Plant No. 1. The only difference would be the wastewater flow rate to the process proposed for option (a), i.e., 250 gpm for Plant No. 2, as compared to 75 gpm for Plant No. 1.

With regard to the economics of the proposed ion exchange system for mercury removal and recovery at Plant No. 2, a recent Akzo Engineering quote (1985 dollars) for a complete plant to handle a 250 gpm wastewater treatment rate is available to permit estimating installed capital cost.[1]

The plant design referred to treats a feed stream with an average 10 ppm mercury content and produces an effluent containing <5 ppb mercury. The adjusted plant cost in 1987 dollars for a 250 gpm feed rate

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1 Personal Communication, Mr. J.B.J. Durville, Akzo Engineering, to plant personnel at Plant No. 2, February 12, 1985.

at Plant No. 2 is estimated as $3.3 million installed. Annual direct operating costs were estimated as $1.2 million per year, including labor, chemicals (including resin replacement), power, and maintenance costs.[1] Present disposal costs of the mercury-bearing waste from wastewater treatment, based on 75 tons per year of K106 waste (containing an average of 2 percent mercury) at $800 per ton[2] delivered to the presently used hazardous waste disposal site, are estimated as $60,000 per year. The recovered value of mercury in the K106 waste would be approximately $78,000 per year. Since the direct operating costs of $1.2 million per year far exceed the savings available, this recycling/reuse option is not considered economically viable.

(e) The use of a retorting process to treat the K106 waste for recovery of elemental mercury and disposal of the mercury-free residue as a delisted non-hazardous waste in a nearby approved sanitary landfill.

Approximately 75 tons per year of wastewater treatment sludge (K106) are generated at Plant No. 2 as a filter cake. From Plant No. 2 characterization data on this material (see above), an average of 2 percent mercury (primarily as mercuric sulfide from the NaSH treatment step) is assumed to be present in this waste. It is proposed to retort this material in a special retort developed for this purpose and in use in a number of other mercury cell chloralkali plants.[3] The retort operates under vacuum and is gas-fired. The mercuric sulfide is assumed to decompose at a temperature of about 1,000°F, forming mercury vapor and SO_2 in the presence of air. Following mercury condensation, the residual vent gases are passed successively through a caustic scrubber to remove SO_2 and an activated carbon column to remove any residual mercury.[4] Based on plant-scale tests of this retort (on a

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1 This estimate is based on Akzo-developed direct operating costs of approximately $0.006/gal of treated wastewater in 1979 dollars increased by 50 percent for equivalent 1987 dollars.

2 Based on discussions with Plant No. 2 personnel, this value would be a worst-case cost.

3 It is assumed that the retort design in question would be available under license.

4 If monitoring of mercury and SO_2 emissions is required, this could be intermittent, using absorption trains to measure these pollutants. It is believed, however that information from a Plant No. 1 conditional delisting petition indicates that an air emissions permit may not be required.

mercurous hydroxide waste at another chloralkali plant), the residue from the retorting step is expected to contain less than 12 ppb mercury and should be able to be delisted by EPA. A simplified schematic of the proposed process is shown in Figure 16.

A retort to recover approximately 1.5 tons per year of mercury (3,000 lb/yr) from 75 tons per year of K106 waste would have to operate intermittently because of the small quantity of waste material involved. It is proposed to accumulate the filter cake initially over a 60-day period, at which time the retort would process this waste during the day shift (8 hours per day) in batches at the rate of about 1,000 pounds per day. The retort system is estimated to cost $100,000 installed. Annual direct operating cost (including fuel, power, labor, and maintenance) for 150 days per year operation, is estimated as $45,000 per year. Recovered mercury value (based on $6 per lb) is $18,000 per year. After achieving a suitable delisting of the retorted material from EPA, available savings in hazardous waste landfill disposal costs would be approximately $60,000 per year.[1] There would thus be an overall net savings in operating this unit (60,000 + 18,000 - 45,000) of $33,000 per year. The payback period in this case would be (100,000/33,000) or 3.0 years, and this option thus may be economically viable. Plant No. 2 should consider this option as a possible alternative to disposal of K106 in the hazardous waste landfill.

Treatment Options

While treatment is not a WM option, Plant No. 2 may want to consider a potentially available treatment alternative to option (e) in order to avoid the capital expenditure involved, as well as the possibility of being required to maintain a complex air monitoring system for potential mercury and SO_2 emissions from the retort used in option (e). A treatment option wherein the K106 waste could be detoxified, enabling it to be delisted and thus be disposed of at a sanitary landfill, may be a technically and economically attractive alternative to the present disposal of K106 in a hazardous waste landfill. One such proposed treatment option is presented below.

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1 It is assumed that the retorted filter cake residue would be disposed of at nominal cost in a local sanitary landfill available for use by Plant No. 2, i.e., combined with the delisted K071 waste that will be disposed of in this landfill (as discussed in Section 4). The $60,000 annual savings is the same amount as discussed under Option (d).

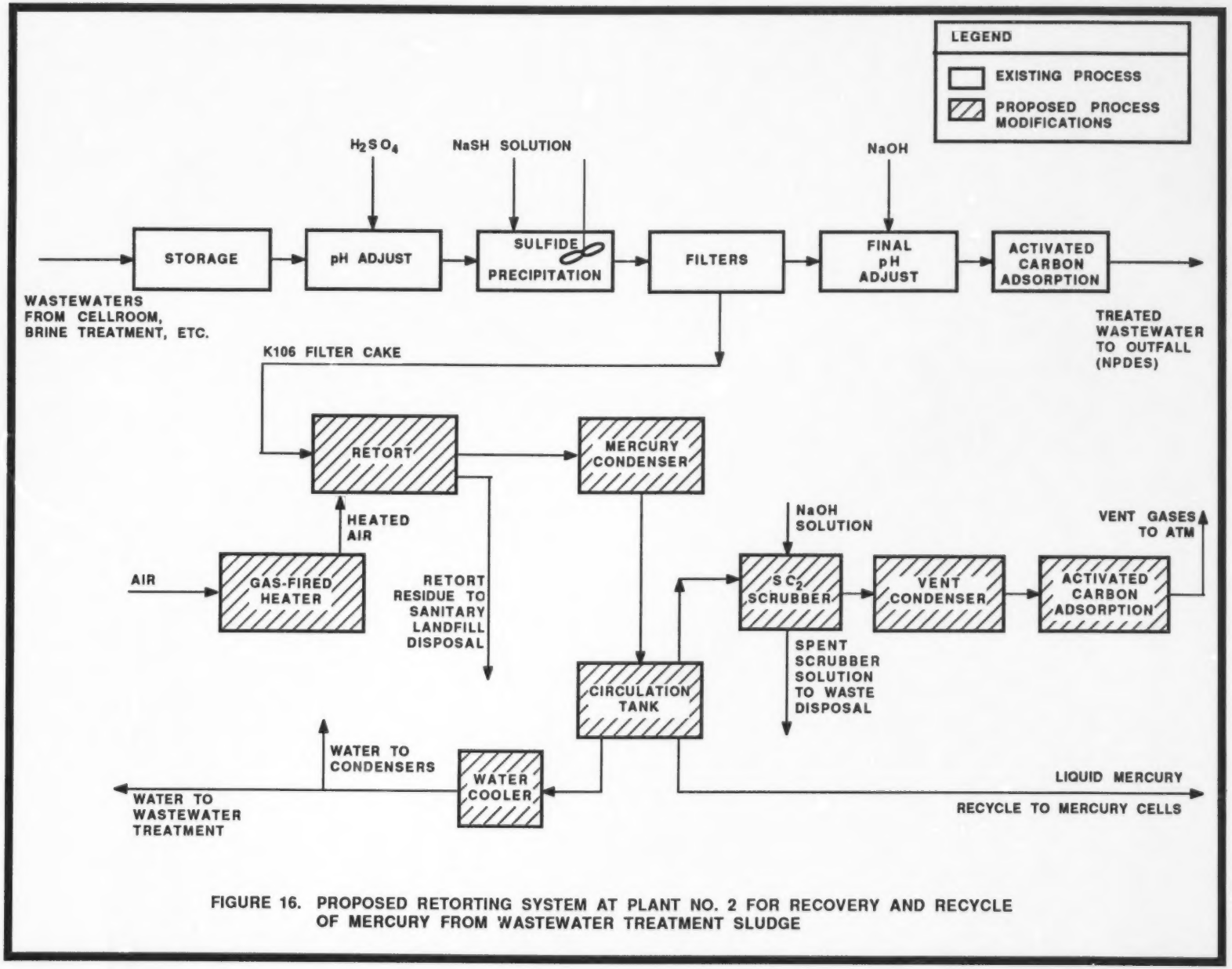

FIGURE 16. PROPOSED RETORTING SYSTEM AT PLANT NO. 2 FOR RECOVERY AND RECYCLE OF MERCURY FROM WASTEWATER TREATMENT SLUDGE

(f) Use of a solidification/stabilization technique to render the K106 waste non-hazardous and permit disposal in a sanitary landfill following suitable delisting.

In this proposed option, the K106 filter cake produced as a result of wastewater treatment at Plant No. 2 would be combined with a cementatious material such as lime kiln or cement kiln dust in order to solidify the waste material in an insoluble matrix, which would then pass the EP-tox test for leachable mercury, i.e., <12 ppb mercury for EPA delisting. Preliminary laboratory work in connection with the current EPA BDAT effort to establish mercury cell chloralkali plant hazardous waste treatment technologies, indicates that it may be possible to immobilize the mercury in the K106 waste, using a solidification/stabilization method. Preliminary results from TCLP leach tests of a blend of one-third by weight lime kiln dust and two-thirds by weight K106 waste, showed leachable mercury to be less that 10 ppb.[1] The solidified material met the 50 psi strength criterion as a low-strength concrete. The results shown here, while preliminary in nature, appear to offer a good possibility for a treatment alternative to disposal of K106 waste in hazardous waste landfills.

Preliminary economics were developed for a solidification/stabilization system based on the results given above. Blending of lime kiln dust and K106 waste would be done on a concrete pad, using a small dedicated concrete mixer (portable type). The blending operation could be done once per week, blending approximately 1 ton of the waste with about 0.5 ton of lime kiln dust. The latter would be stored in a storage building holding about 3 months supply (5-10 tons) of the latter material in bags. The blended material would be allowed to cure on a concrete storage pad for 1 to 2 months prior to being shipped offsite to the nearby sanitary landfill available to Plant No. 2.[2]

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1 Personal Communication, Mr. M. Arozarena, PEI, Inc., Cincinnati, Ohio, April 29, 1987. The K106 waste was produced by wastewater sulfide treatment at the Vulcan Chemical Plant, Port Edwards, Wisconsin, chloralkali facility. This technique would have to be applied to other K106 wastes and be given more in-depth testing to establish its viability.

2 This material, following submission of suitable TCLP leachate data to EPA, would be delisted and thus be suitable for disposal in a sanitary landfill. It is assumed that a permit would be required to operate as a TSD facility in order to carry on this operation.

Total installed cost for a suitable prefabricated storage building to hold the lime kiln dust, a small portable concrete mixer, and a concrete pad area for blending and curing the solidified K106 waste, is estimated as $15,000. It is believed that there is adequate space adjacent to the K106 waste generation area to perform these operations. Annual operating costs (including labor, lime kiln dust, fuel, and maintenance) is estimated as $10,000 per year. Savings in disposal cost for the delisted K106 would be approximately $55,000 per year based on disposal in the nearby sanitary landfill. Overall annual savings available if the proposed treatment option was implemented, is estimated as $45,000 per year, with a payback period of approximately 4 months. This option appears to be worthy of further evaluation, including research and development to establish the appropriate operating parameters for the solidification/stabilization reaction involving K106 waste and lime kiln dust (or other suitable solidification/stabilization material).

Summary of Postulated Options for Minimization of K106 Waste at Plant No. 1 and Plant No. 2

A total of three recycle/reuse options as well as two detoxification treatment options were developed by the audit team for listed waste K106 at Plants No. 1 and 2. Table 13 summarizes these options and results of the preliminary evaluation by both the audit team and respective plant personnel. One WM option (recycle/reuse) involving retorting of K106 waste for mercury recovery and one treatment option (detoxification treatment of K106 using stabilization/solidification) appear worthy of further evaluation for minimization of this waste at both Plants No. 1 and 2.

Summary and Discussion

The K106 waste generated at mercury cell chloralkali plants is a low-volume waste, variable in quantity, and ranging between 10 and 100 tons per year depending on plant size. This material (wastewater treatment sludge) typically contains approximately 50 percent water, with the balance inerts (diatomaceous earth and carbon) with mercury content-typically in the form of the insoluble sulfide (Plant No. 1 is an exception in its use of hydrazine as the mercury precipitant) ranging from 0.5 to 5 percent. The wastewater from which this sludge derives (after the precipitation treatment step) is a relatively small stream, typically in the 50 to 100 gpm range, with 5 to 10 ppm levels of mercury.

Source reduction options are not available to reduce or eliminate the wastewater; recycle/reuse options for the low levels of mercury in the wastewater, i.e., ion exchange wastewater are not economically feasible for primary removal of mercury. Ion exchange or activated carbon treatment has been used as a polishing step following primary treatment of wastewater by processes such as sulfide or hydrazine precipitation.

Table 13. Summary of Postulated Options for Minimization of Listed Waste K106 at Plants No. 1 and No. 2

Option	Description	Type of option	Advantages	Disadvantages	Potential savings over present cost of waste disposal ($/yr)
(a)	Ion exchange treatment of raw wastewater for removal and recovery of mercury (applicable to both Plants No. 1 and No. 2)	Recycle/ reuse	Process demonstrated commercially. Capable of achieving necessary mercury level in effluent discharged under NPDES. Mercury can be recycled to mercury cell system in ionic form without having to reclaim the metal.	Extensive pretreatment of brine required in order to safeguard resins capacity to remove mercury. Unacceptable economics.	-
(b)	Retorting of K106 waste to recover metallic mercury for recycle to mercury cells at Plant No. 1	Recycle/ reuse	Process demonstrated commercially for hydrazine-based wastewater treatment sludge. Capable of producing residue low enough in mercury to allow delisting by EPA. Metallic mercury recovered by retorting can be recycled to mercury cells.	Unacceptable economics unless recovery process throughput can be increased substantially. Plant No. 1 is applying for conditional delisting of this waste in spite of negative economics.	-
(c)	Solidification/ stabilization of K106 waste in an insoluble matrix followed by disposal by Plant No. 1 as a non-hazardous waste (once delisted by EPA)	Treatment	Simple, inexpensive process to install and operate (favorable payback period). Once waste is delisted by EPA, can be placed in a nearby sanitary landfill.	Process not commercially proven. Will require a large body of operational data to obtain EPA approval for delisting.	4,500

Table 13. (Continued)

Option	Description	Type of option	Advantages	Disadvantages	Potential savings over present cost of waste disposal ($/yr)
(d)	Same as (b) for Plant No. 2	Recycle/ reuse	Process has been in commercial use in several mercury cell chloralkali plants for sulfide-based wastewater treatment sludge. Recovered metallic mercury can be recycled to mercury cells. Capable of producing residue low enough in mercury to allow delisting by EPA. Could have favorable economics (payback period) due to potentially high cost of K106 disposal once it cannot be combined with K071 waste (when the latter is delisted at Plant No. 2) for shipment to the hazardous waste landfill.	May require extensive stack emissions monitoring system for mercury and SO_2 emissions.	60,000
(e)	Same as (c) for Plant No. 2	Treatment	Same as (c).	Same as (c).	55,000

In summary, the results of WMAs conducted at Plants No. 1 and No. 2 by the EPA-sponsored audit indicated that only one WM option is available for minimization of K106 waste at mercury cell chloralkali plants: retorting of K106 waste sludge (in the form of a filter cake) for mercury recovery and recycle to the process with delisting and disposal of the retort residue in a local sanitary landfill. This option is technically well-proven and may be economically feasible at Plant No. 2. Plant No. 1 appears ready to adopt this option in order to succeed in ultimately having this waste delisted by EPA, irrespective of process economics. Adoption of this option at Plant No. 2 can potentially result in savings (as compared to the present cost of disposal in a hazardous waste landfill) of $60,000 annually with a payback period of about 3 years.

With only one WM option available to Plants No. 1 and 2 for K106 waste minimization, the audit team investigated the possibility of using a treatment option to detoxify this waste. Current preliminary EPA BDAT investigations indicate that a solidification/stabilization technique using lime kiln dust can produce a solidified waste that, upon TCLP extraction, shows leachable mercury in the <12 ppm range, offering the potential for EPA to delist the stabilized waste. A commercial process incorporating this procedure would show a $4,500 and $55,000 annual savings in waste disposal costs, respectively, for Plant No. 1 and Plant No. 2 with payback periods in the 3-year range. Additional research and development will be required to establish mercury leachability results on a wide variety of K106 wastes, as well as the required operational parameters for optimum stabilization results.

SECTION 6

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